



Lawrence Livermore National Laboratory  
University of California  
Livermore, California 94551

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# Historical Case Analysis of Chlorinated Volatile Organic Compound Plumes

## *Primary Authors*

Walt W. McNab, Jr.  
David W. Rice  
Jacob Bear<sup>1</sup>  
Richard Ragaini  
Cary Tuckfield<sup>2</sup>  
Curt Oldenburg<sup>3</sup>

## *Contributing Authors*

Gregory Bartow<sup>4</sup>  
Mike Brown<sup>5</sup>  
Patrick Haas<sup>6</sup>  
Christina Hubbard<sup>7</sup>  
Janet Jacobsen<sup>3</sup>  
Michael Kavanaugh<sup>7</sup>  
Douglas Mackay<sup>8</sup>  
William Mason<sup>9</sup>  
Thomas McKone<sup>10</sup>  
Michael Pound<sup>11</sup>  
Heidi Temko<sup>12</sup>

**March 8, 1999**

- 1 Technion-Israel Institute of Technology
- 2 Savannah River Technology Center
- 3 Lawrence Berkeley National Laboratory
- 4 San Francisco Bay Regional Water Quality Control Board
- 5 U.S. Department of Energy
- 6 U.S. Air Force Center for Environmental Excellence

- 7 Private Consultant
- 8 University of Waterloo
- 9 Oregon Department of Environmental Quality
- 10 University of California, Berkeley
- 11 U.S. Naval Facilities Engineering Command
- 12 California State Water Resources Control Board



**Environmental Protection Department**  
Environmental Restoration Division

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## Preface

There are several national initiatives that continue to re-evaluate chlorinated volatile organic compound (CVOC) cleanup processes. These include efforts by the United States Environmental Protection Agency (US EPA) to reconsider the manner in which CVOC toxicity factors are developed; efforts by many investigators to evaluate the mechanisms and impacts of natural attenuation at individual sites; and efforts by the Department of Energy (DOE), the Department of Defense (DOD), and the US EPA to evaluate the use of enhanced natural attenuation during CVOC cleanup and to demonstrate new remediation technologies. Missing from these initiatives is a cross-cutting evaluation of the large amounts of CVOC historical case data that are available.

This document describes the findings and conclusions resulting from a study of nationwide historical case data gathered from sites with groundwater contaminated by CVOCs. The purpose of this initiative (the "Initiative") is to use a statistical perspective and data from multiple sites to evaluate the hydrogeologic, biogeochemical, and physiochemical factors affecting the extent and growth behavior of CVOC plumes in groundwater. This evaluation is important because of the significant role that plume behavior plays in the management of human health, environmental decision making, and resource risk evaluation.

The CVOC Initiative is a cooperative partnership between a variety of organizations and agencies involved in the cleanup of CVOC plumes. The Environmental Council of States, Interstate Technology and Regulatory Cooperation (ITRC) working group serves as a link to state regulatory bodies. The US EPA, DOE, US Navy, US Air Force, industry, and ITRC member states have provided CVOC historical case data in support of this Initiative.

The data management, statistical analysis, and modeling efforts conducted within the framework of the Initiative were performed by a team of scientists and environmental professionals from Lawrence Livermore National Laboratory (LLNL), Lawrence Berkeley National Laboratory (LBNL), and Savannah River Technology Center (SRTC). On behalf of DOE, LLNL has served as the overall Initiative Coordinator. Throughout the project, ITRC member states have been regarded as the appropriate entities to consider the development of any recommendations that would be warranted on the basis of the scientific evaluation of the historical case data, as presented here.

As part of this Initiative, two groups were formed: a Working Task Force (WTF) and a Peer Review Panel (PeerRP). The WTF focused on the technical issues of historical CVOC case data collection and analysis as well as preparing draft findings and conclusions based on the data analysis. The PeerRP was called upon to review key deliverables, raise technical issues, and review and comment on draft findings, conclusions, and recommendations. The members of the WTF are:

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- Richard Ragaini, Ph.D., Lawrence Livermore National Laboratory,
- \*David Rice, Lawrence Livermore National Laboratory,
- Heidi Temko, California State Water Resources Control Board,
- Cary Tuckfield, Ph.D., Savannah River Technology Center, Westinghouse Savannah River, Co.

\* CVOC Historical Case Analysis Project Director

# Executive Summary

## Overview of the Study

Knowledge about the general patterns in behavior of chlorinated volatile organic compound (CVOC) plumes, their transformation daughter product plumes, and relationships between plume behavior and site variables is essential to managers and decision-makers engaged in CVOC plume investigation and remediation. By analyzing populations of plumes, likely CVOC plume behavior scenarios can be better understood.

The present study represents an attempt to understand the factors affecting the behavior of CVOC plumes in groundwater from a broad, statistically oriented perspective. One of the key issues in using historical case data is the often-unknown quality of the data, and yet these data are typically used as the basis for site cleanup decision making. Thus, a key goal of this study is to evaluate a large population of historical CVOC case data and evaluate which aspects of CVOC plume behavior and CVOC risk management can be supported by historical case data. It is reasonable to expect that by analyzing site-specific field data from a relatively large number of CVOC releases, the relationships between CVOC plumes and site characteristics can be identified, albeit on a statistical basis. As such, the general findings of this study are not necessarily applicable to any individual site. However, managers of specific sites will benefit from the analysis and its conclusions, as their understanding of plume behavior is enhanced through an examination of data from many sites. It is believed that focusing on the major factors influencing plume behavior will increase the efficiency of planning site investigation and cleanup operations.

Specifically, the following general questions involving the applicability of historical case data to CVOC risk management are addressed:

1. Can historical case data be used to predict CVOC plume behavior?
2. What are key uncertainties associated with evaluating CVOC plume behavior using historical case data and what other types of data are needed?
3. How may CVOC historical case analysis be used in CVOC cleanup decision-making?

A number of more specific questions of interest to researchers and managers of CVOC cleanup regarding the factors that are related to CVOC plume behavior are also addressed by this study. These questions include:

4. How often is a dense non-aqueous phase liquid (DNAPL) inferred to be present at sites within the CVOC historical data set and what is the relationship of inferred DNAPL presence to the plume length at a given site?
5. How often are transformation processes encountered in CVOC plumes in the data set and what are the relationships between the indications of transformations and plume length?
6. Do daughter product plumes behave differently compared to parent CVOC plumes?

7. What is the relationship of fuel hydrocarbon co-contamination to CVOC plume behavior?

## Methodology

The primary analysis approach during this study was to identify and quantify trends and relationships in the data between plume characteristics (e.g., plume length) and site hydrogeologic, biogeochemical, and CVOC physiochemical variables using correlation analyses and population inference tests. To conduct the study, procedures for data collection and analysis included the following specific tasks:

1. Candidate sites were screened using a site checklist. Sites were accepted for inclusion in the study if: (a) data were available from at least six monitoring wells over a three-year monitoring period prior to remediation, (b) site plumes did not significantly daylight, (c) site plumes were not significantly affected by pumping in nearby wells, and (d) interpretation of plume length was not complicated by multiple CVOC sources. Once a site passed the screening and was accepted in the study, CVOC historical monitoring data were obtained electronically, and hydrogeologic data were extracted from site reports.
2. Mean values were estimated for site hydrogeological variables, such as groundwater velocity. Different variables required different approaches to quantify mean site values. For example, in the case of hydraulic conductivity, a representative mean site value was quantified by utilizing the geometric mean of values reported for individual monitoring wells through pumping tests or slug tests. Reductive dehalogenation potential was treated as a categorical variable, defined by the presence of certain reductive dehalogenation daughter products and supported by an analysis of trends in groundwater geochemistry.
3. The key plume characteristics, plume length and plume length growth rate, were estimated for all individual CVOCs at each site in the study. Plume lengths were estimated using an algorithm that used CVOC concentration data to systematically quantify the distance from the location of the reported maximum CVOC concentration in a plume to a distal 10-ppb, 100-ppb, or 1000-ppb contour. Relative plume growth rates were estimated on an individual CVOC basis using time-series analysis of plume data from individual sites.
4. Statistical analyses were performed to identify relationships between plume length and site hydrogeological variables, the physiochemical properties of individual CVOCs, and the identified biogeochemical transformation categories. Statistical tests included analysis of correlation, comparison of population means, and the development of a general linear statistical model.
5. Probabilistic plume modeling was employed to provide a mathematical conceptual framework to relate observed correlations to fate and transport mechanisms. The mathematical modeling provided an inferential line of reasoning that was used as a basis of comparison to the statistical reasoning used during the analyses of the CVOC field data. Agreements between the two approaches provided validation of the study findings.

The study involved the collection and analysis of data from 65 sites representing a variety of hydrogeologic settings and release scenarios (e.g., large industrial facilities, dry cleaners, and landfills). Data collection involved a variety of federal and state agencies and included participation from the U.S. Department of Defense, the Department of Energy, and private industry. Plumes were defined per CVOC per site, yielding a total of 247 plumes delineated by the 10-ppb contour and subsets of 134 plumes and 58 plumes delineated by the 100- and 1000-ppb contours, respectively. A total of 16 different CVOCs were included in the study.

## Findings

An evaluation of the CVOC historical case data collected to date found the following general characteristics:

- The contaminant chemistry was generally found to be the most complete of the data types reviewed. Data on hydraulic conductivity and organic carbon content of soils and groundwater were less systematically collected and/or reported. Theoretically, these parameters should be key to understanding the fate and transport of subsurface contaminants.
- As an aggregate population, CVOC plume lengths are approximately lognormally distributed, although with some deviations. In particular, the frequency of small plume lengths appears to be under-represented in this data set based on a lognormal probability distribution model.
- Among the sites in this study, the longest CVOC plume lengths from each site are also lognormally distributed. Among these plumes, the median CVOC plume length was approximately 1600 ft, and 90% of the CVOC plumes in this study were less than approximately 6300 ft in length.
- There are no statistically significant differences between CVOC species with regard to their log-transformed 10-ppb plume lengths, including likely transformation daughter products such as *cis*-1,2-DCE and vinyl chloride.

Correlation analysis and population inference tests revealed a number of trends in the field data. These include:

- Plume lengths are positively correlated with maximum historical CVOC concentrations and mean groundwater velocity at each site.
- Based on the observed maximum historical concentrations, approximately 40% of the TCE plumes may be associated with DNAPL based on a 1% solubility limit rule-of-thumb, and approximately 10% of the TCE plumes may be associated with a DNAPL based on a 10% rule-of-thumb. Based on these solubility limit rules-of-thumb, the presence of DNAPL is suggested in a majority of cases where a 1000-ppb TCE plume can be defined.
- The effects of reductive dehalogenation on the plume length are measurable, but only when the influences of source area mass (maximum groundwater concentration) and groundwater velocity are factored out. Plume lengths adjusted for these variables are shorter when there is strong evidence of reductive dehalogenation. These results suggest

that the role of transformation processes in influencing CVOC plume lengths is relatively subtle. There is also evidence that plumes at sites exhibiting strong reductive dehalogenation show less plume growth than those from other sites.

- Large daughter product plumes do not commonly extend a large distance downgradient of the parent product plumes.
- The statistical association between fuel hydrocarbons, elevated bicarbonate alkalinity, and the presence of vinyl chloride plumes provides circumstantial evidence that fuel hydrocarbon co-contamination may be an important factor in the reductive dehalogenation of CVOC plumes in the historical case analysis data set. Elevated manganese concentrations at sites with vinyl chloride plumes is consistent with the presence of an anaerobic environment at these sites.
- Variability in maximum concentration between sites is positively correlated with literature derived CVOC-specific organic carbon partitioning coefficients. In addition, some positive correlation may exist between the Henry's Law constant and variability in maximum concentration between sites. Furthermore, there is a possible correlation between plume length and the Henry's constant once factors such as source strength and groundwater velocity are factored out. Although these relationships are statistically significant and are consistent with idealized conceptualizations of plume behavior, these results must be viewed as preliminary in nature. Further studies must be conducted to independently confirm these observations.

Monte Carlo simulation, using an analytical plume model and inferred probability distributions of hydrogeologic variables, was used to generate populations of synthetic plumes. Application of the same analytical approaches used for the field data to the synthetic plume data, yielded similar results in terms of plume length relationships.

## Conclusions

This study provides the first statistical analysis of data from a relatively large population of CVOC plumes. From this analysis, the following conclusions result:

- This study demonstrates that broad trends in relationships between plume behavior and key site variables can be determined through the statistical analyses of historical field data from a large number of sites. This finding is important because it demonstrates that: (1) specific hydrogeologic conditions and contaminant release scenarios at individual sites are not so unique that expected overall trends in the data are completely obscured, and (2) useful average values for site variables such as hydraulic conductivity and groundwater velocity can be quantified in most situations.
- This study also shows that statistical methods, such as general linear models and comparison of probability distributions of plume length indices<sup>1</sup>, are useful to quantify expected relationships between plume length and site and CVOC variables within a population of CVOC plumes. In addition, they provide population statistics that may be used to bound the uncertainty inherent in expected plume behaviors.

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<sup>1</sup> Plume length index is defined as the plume length divided by the groundwater velocity and by the maximum groundwater concentration of the contaminant.



- This study provides quantitative confirmations that plume behaviors can be grouped and that these groupings are based on expected hydrogeologic processes.
- One of the major features of this study is that its analyses and conclusions are based primarily on actual field observations, i.e., data from actual CVOC plume historical cases. At present, there is no evidence that the historical case data can be used predictively outside the range of data reviewed. The strength of the conclusions arising from statistical analyses of the CVOC data are dependent upon data set characteristics, particularly the representativeness and the quality of the data. It must be noted that the plume length distributions, relative plume growth rates, and the types of CVOCs involved are reflective of the 65 sites in the project database exclusively. There is no way of ascertaining whether or not these distributions present an unbiased sample of the entire population of CVOC plumes across the U.S. without conducting a much larger survey on a vast scale. As more data are added to the CVOC historical data set, representativeness will be enhanced.
- Based on the rules-of-thumb as indicators of free-phase CVOCs, the results of this study suggest that the DNAPL may be influencing plume behavior to a certain extent, although, not in the case of daughter product species, e.g., *cis*-1,2-DCE, vinyl chloride, and possibly 1,1-DCA and 1,1-DCE in some cases. It must be emphasized that these inferences are based entirely on very general rules-of-thumb that have been established in the contaminant hydrology literature. In reality, there is no direct way of ascertaining whether or not DNAPLs are present at the sites given the data provided for this study. However, the relationships between plume length and reported maximum concentration are likely to reflect the overall strength of the source term, which may in turn be influenced by the presence or absence of DNAPL as well as the capacity for any residual DNAPL to be actively leached into groundwater.
- An important conclusion of this study is that the presence of a vinyl chloride plume indicates that reductive dehalogenation may be playing a role in reducing the extent of CVOC plumes at approximately one-third of the sites examined. In contrast, the presence of a *cis*-1,2-DCE plume in the absence of a vinyl chloride plume appears to indicate reductive dehalogenation rates that are insufficient to effectively reduce the extent of CVOC plumes at a site. Little evidence was found in the data to suggest that plume lengths and plume growth rates are substantially affected by reductive dehalogenation in these circumstances.
- Another important conclusion is that CVOC transformation rates through dehalogenation exert less impact on plume length than source strength and groundwater velocity. Thus, plumes with weaker source strength and slower groundwater velocities may be better candidates for the application of natural attenuation remedies.
- The statistical results of the CVOC historical case analysis suggest that the association between fuel hydrocarbons and reductive dehalogenation may be widespread. It is important to recognize, however, that the West Coast-bias in the site representation in the data set may influence these results. For example, sites from the eastern U.S., characterized by higher precipitation and therefore a greater preponderance of vegetation, may be characterized by larger quantities of natural organic carbon which would be

available to facilitate reductive dehalogenation. In such instances, the influence of fuel hydrocarbon co-contamination may be less pronounced.

## Discussion and Recommendations for Future Work

It is clear that variability is a fundamental characteristic of CVOC sites and that conclusions stemming from the current study are general and should not be strictly applicable at any specific site. Although the emphasis in this study is on examining correlations between plume length and hydrogeologic variables, it is apparent that there is enormous variability in both plume length and maximum concentration.

Continued data collection is recommended because a more comprehensive data set would shed light on some of the questions not answered completely in this present study. These questions include:

- Are there significant differences in plume behavior across different geographic hydrogeologic regimes (e.g., as specified in Heath, 1984)?
- Is there a dependence of plume behavior on climatic factors such as mean annual rainfall, evapotranspiration rate, or vegetative cover at the site?
- What is the quantification of statistical relationships between site natural organic carbon content and (1) retardation of plume length or normalized plume length and (2) reductive dehalogenation? With regard to reductive dehalogenation in particular, a comparison of the roles of natural organic carbon and anthropogenic carbon sources (e.g., fuel hydrocarbons) would be of significant interest.
- Are there differences in the relationships of plume behavior to site variables, particularly the classes of plumes specifically excluded from this study, e.g., plumes that daylight. The use of exclusion criteria may systematically under-represent very short and very long plumes in the data set.

In summary, this study sets a precedent for future historical case analysis studies that might include:

1. A more detailed analysis of retardation phenomena contingent upon availability of soil organic carbon data.
2. Geostatistical analyses of plume spatial moments to include dispersion (in three dimensions) as a variable.
3. Development of a significantly expanded data set (i.e., hundreds of sites) which would allow subsets of site classes to be evaluated separately and then be compared to one another. The ultimate goal of such follow-on studies should be to develop a comprehensive statistical model for plume behavior.

This statistical model could provide:

1. Individual site investigators with a plume reference model against which a given plume may be compared and used to identify anomalous behavior.
2. Regulatory agencies with an integrated survey of plume behavior under a variety of conditions.

3. Validation for theoretical models and anecdotal studies of plume behavior within a probabilistic conceptual framework.

The results of this historical case analyses may be used by a site manager to develop initial site conceptual models and help focus characterization resources on data that will be most useful in confirming or denying conceptual model hypotheses. In addition, the study provides information on the types of data that are not currently being collected that should be collected in the future, e.g., organic carbon analysis.



# **1. Introduction**

## **1.1. Background**

Knowledge about the general patterns in behavior of chlorinated volatile organic compound (CVOC) plumes, their transformation daughter product plumes, and relationships between plume behavior and site variables is essential to managers and decision-makers engaged in CVOC plume investigations and remediation. By analyzing populations of plumes, likely CVOC plume behavior scenarios can be better understood.

To date, CVOC groundwater plume behavior has been studied at a large number of individual sites, but has never been evaluated through a systematic statistical analysis of available data on a relatively large number of existing plumes. Individual site studies indicate that each site features its own individual characteristics (e.g., geological structure, aquifer parameters, transport, and chemical and biological transformation mechanisms) which, in turn, produce a plume that has its own particular morphological features (e.g., length, depth, and rate of growth). Unfortunately, because field data are often sparse as a result of economic and sampling constraints, a thorough, detailed understanding of plume behavior at a given site is more the exception than the rule. Nevertheless, the same flow, transport, and transformation mechanisms influence essentially all CVOC plumes, although at a magnitude that may vary greatly from site to site. Thus, it is reasonable to expect that by analyzing site-specific field data from a relatively large number of CVOC releases, the relationships between CVOC plumes and site characteristics can be identified on a statistical basis. The key is to gather and analyze data from a large number of plumes.

Several previous studies have attempted to compare CVOC plume behavior using a limited number of sites, focusing primarily on the effectiveness of the groundwater pump-and-treat techniques. Doty and Travis (1991) evaluated 16 sites, US EPA evaluated 19 sites (Keely, 1989; US EPA, 1989) and 24 sites (US EPA, 1992), the National Research Council (1994) evaluated 72 sites, and Bartow and Davenport (1995) evaluated 37 sites. None of these previous studies has attempted to evaluate CVOC plume extent and growth behavior, which are primary goals of this study, nor did most of these previous studies use a statistically meaningful data set.

## **1.2. Project Objectives**

The present study represents an attempt to understand the factors affecting the behavior of CVOC plumes in groundwater from a broad, statistically oriented perspective. One of the key issues in using historical case data is the often-unknown quality of the data, and yet these data are typically used as the basis for site cleanup decision making. Thus, a key goal of this study is to evaluate a large population of historical CVOC case data and evaluate which aspects of CVOC plume behavior and CVOC risk management can be supported by historical case data. Further, knowing which key variables are significantly related to aggregate plume behavior, and which are less important, allows knowledgeable decisions to be made to the allocation of resources to site characterization and to remedial activities.

Because the results of any such evaluation are necessarily presented in a probabilistic format, they will mainly serve those persons interested in broad trends in CVOC plume behavior across many sites. As such, the general findings of this study are not necessarily applicable to any individual site. However, managers of specific sites will benefit from the analysis and its conclusions, as their understanding of plume behavior and the major factors that are related to plume behavior will have been enhanced through an examination of data from many sites. It is believed that focusing on these major factors will increase the efficiency of planning site investigation and cleanup operations.

Specifically, the following general questions involving the applicability of historical case data to CVOC risk management are addressed:

- Can historical case data be used to predict CVOC plume behavior?
- What are key uncertainties associated with evaluating CVOC plume behavior using historical case data and what other types of data are needed?
- How may CVOC historical case analysis be used in CVOC cleanup decision-making?

A number of more specific questions of interest to researchers and managers of CVOC cleanup regarding the factors that are related to CVOC plume behavior are also addressed by this study. These questions include:

- How often is a dense non-aqueous phase liquid (DNAPL) inferred to be present at sites within the CVOC historical data set and what is the relationship of inferred DNAPL presence to the plume length at a given site?
- How often is there evidence of transformation processes in association with the CVOC plumes in the data set and what are the relationships between the indications of transformations and plume length?
- Do daughter product plumes behave differently from parent CVOC plumes?
- What is the relationship of fuel hydrocarbon co-contamination to CVOC plume behavior?

## **2. Methods**

### **2.1. Overview of Project Data Analysis Approach**

In principle, the behavior of a contaminant plume in an aquifer is affected by a number of variables. These include the geologic features of the aquifer, the hydraulic properties of the porous medium (including its spatial variability), the chemical composition of the indigenous water, the chemical nature of the contaminant of interest and its interactions with other aqueous constituents, the geologic substrate, the local microbiota, etc. See Appendix A, Sections A-1 and A-2 for additional details. To understand the factors affecting the behavior of CVOC plumes in groundwater from a broad, statistically oriented perspective, the basic process of the CVOC historical case analyses was to first define plume characteristics such as plume length. The next step was to assess the degree of correlation of these plume characteristics with mechanisms and processes of CVOC transport and transformation as manifested by hydrogeologic, biogeochemical, and physiochemical variables.

To provide guidance in the pursuit of the project objectives, a set of general hypotheses were developed prior to the collection and analysis of the data. These hypotheses were established to provide focus and scope to the project and to aid in developing the appropriate testing methodologies. Other hypotheses were developed and tested during the course of the data analysis. The initial hypotheses include:

- Relationships between plume characteristics and site and CVOC physiochemical variables that would be expected to influence plume behavior (e.g., site hydraulic conductivity, biotransformation rate, volatilization potential) should not be completely masked by variability in site-specific features. Examples of such features include the presence of preferential subsurface flow pathways or conduits, multiple hydrostratigraphic units, or a complex release history. Rather, the variability in the site-specific features will simply contribute random noise in the statistical relationships being examined.
- CVOC plumes characterized by evidence of transformation processes will exhibit different plume behavior compared to CVOC plumes without this evidence. In particular, plumes undergoing reductive dehalogenation, as well as those composed of 1,1,1-TCA (a compound which transforms abiotically in groundwater environments), would be expected to be relatively shorter in length. An important assumption of this hypothesis is that plumes undergoing reductive dehalogenation can be distinguished in a systematic way from those that are not.
- Among the physical and biogeochemical variables that could be quantified for sites and CVOCs in the study, groundwater velocity and indications of transformation processes should be expected to be significantly related to plume characteristics. Other variables (e.g., age of the plume, depth to groundwater, retardation coefficient) would be weakly related to plume characteristics by comparison. This hypothesis is based upon previous experiences and best professional judgment of the investigators.

Once the CVOC historical data base was established (See Section 3.2, below), analysis proceeded according to four general steps:

1. Mean values were estimated for the site hydrogeological variables: hydraulic conductivity, groundwater velocity, and geochemical indicator parameters. Different variables required different approaches in deriving site specific means. For example, a representative site mean hydraulic conductivity was derived from the geometric mean of hydraulic conductivity values reported for individual monitoring wells through pumping tests or slug tests. Mean hydraulic gradient was derived based on mean values reported in consultant reports or was estimated from potentiometric surface maps.
2. Reductive dehalogenation activity was categorized according to the presence of certain CVOC reductive dehalogenation daughter products, supported by an assessment of the groundwater geochemical indicators (see discussion in Appendix A, Section A-2, Transformation of CVOCs). Concentrations of geochemical indicators of transformation, such as chloride ion concentrations, were estimated using the 90<sup>th</sup> percentile concentration from each site and geochemical indicator compounds. In evaluating the data, hydrogeological variables provided in consultant reports were taken at face value.

3. The primary plume characteristics used in this study are plume length and plume length growth rate. These characteristics were estimated for each CVOC at each site in the study. Plume length was defined by the distance from the location of the maximum CVOC concentration in the plume (the presumed source area) to the most distal 10 part-per-billion (ppb), 100-ppb, or 1000-ppb isoconcentration contour location. This estimation was made using an algorithm that systematically quantified plume length based on analysis of site-specific spatial distributions of CVOC concentration data. A description and discussion of the plume length algorithm is presented in Appendix B. Individual CVOC plume growth rates were estimated using time series analysis of plume data from a given site.
4. Statistical analyses were performed to identify relationships between plume length and site hydrogeological variables, reductive dehalogenation activity, and physiochemical properties of individual CVOCs. Statistical tests included analysis of correlation, comparison of population means, and the development of a general linear model (GLM). The GLM was used to quantify the contributions of site variables to the observed variance in plume characteristics. This provided a means for comparing individual plume characteristics to other plumes from similar hydrogeologic settings and to facilitate the identification of anomalous plume behavior or morphology. Details of the application of the GLM to the CVOC historical case data set are presented in Appendix C.

Any study using statistical analyses of field data would be expected to yield findings that are entirely empirical in nature. Therefore, it is important to view the results of the CVOC historical case data analysis within the framework of a mathematical conceptual model of plume behavior. In principle, predictions of plume behavior could be prepared using theoretical models that describe plume evolution on the basis of the fundamental laws governing flow and transport in porous media. Such models include the consideration of factors (e.g., hydraulic conductivity, hydraulic gradient, transformation and adsorption coefficients) that determine the behavior of a contaminant plume at a specific site. Once these factors and associated variability are known for a given site, the plume's behavior at that site can be predicted theoretically. Unfortunately, under field conditions, we are confronted with two fundamental difficulties:

1. At most sites, there is no practical way to obtain information on all the relevant site-specific factors influencing the plume. This is especially true with regard to chemical and biological transformations that may have a pronounced effect on the CVOC plumes.
2. Uncertainty exists with respect to practically all factors and associated variability that affect plume characteristics at any particular site, due to the heterogeneity of the domain, lack of information on boundary conditions, etc.

To address these difficulties, probabilistic plume modeling was employed during the application of the mathematical conceptual model, parallel to the analyses of field data. This probabilistic plume modeling involved the use of a Monte Carlo simulation technique to generate a large number of synthetic plumes for cases for which analytical solutions to the transport equation are available. Probability distributions of the site hydrogeologic variables were obtained whenever possible from the site data collected in the study. Essentially, this modeling effort produced a parallel, synthetic data set to compare to the field data.



## 2.2. Definitions and Assumptions

During the analysis of the CVOC historical case data, a *variable* was defined as a measurable quantity that describes some feature of the plume itself or its local hydrogeological environment. The former is referred to as a “dependent”, or “plume characteristic variable”, while the latter is referred to as an “independent site variable”. The magnitude of a plume characteristic variable presumably is related to, or dependent upon, the magnitude of one or more independent site variables where the average of each variable changes from site to site. Variables can be grouped as:

Plume characteristic variables (i.e., dependent variables). These include plume length and plume growth rate. Here, *plume length* is defined, per CVOC, as the distance from the well where the maximum historical concentration was measured to the most distal location of the concentration contour of interest. Where possible, plume lengths were developed for three isoconcentration contours: 10 ppb, 100 ppb, and 1000 ppb. These isoconcentration contours were chosen because they addressed the detection limits typically reported as well as the ranges of concentrations encountered at the majority of sites. The CVOC concentration data can be quite variable at low concentrations, and projected CVOC plume boundary estimations at concentrations less than 10 ppb can be strongly influenced by this variability. Thus, plume lengths defined by concentrations less than 10 ppb were not quantified.

In the context of this study, plume length and plume growth rate, i.e., change in plume length as a function of time, are highly idealized concepts of plume behavior given the complex morphology expected of subsurface groundwater plumes. Nevertheless, given the limited spatial resolution provided by the monitoring well networks at most of the sites in the study, and given the number of sites involved, such a simplified model is appropriate in the context of this study.

In addition, while it is recognized that detailed delineation of CVOC plumes often involves the vertical dimension, it is assumed in this study that concentrations may be averaged across the vertical extent of the aquifer(s), so that plumes are effectively treated as two-dimensional bodies. This assumption, which must be placed in context of the overall goals of the study, is based on the common observation that the horizontal extent of most plumes usually exceeds the vertical extent by a large factor.

In this study, three different types of independent variables were evaluated for their possible relationship to plume characteristics, principally plume length:

Hydrogeologic variables (i.e., independent site variables). These include (among others): source strength and groundwater velocity.

- *Source strength.* The magnitude of the reported maximum concentration within a CVOC plume was assumed to reflect the strength of the plume’s source. In the case of parent CVOCs, this may involve DNAPL dissolution, whereas for daughter product plumes the maximum concentration may be indicative of the area where the majority of the mass transformation is taking place. The spatial location of the reported maximum concentration was used to estimate the best approximation of the location of the CVOC source.
- *Groundwater velocity.* Mean groundwater velocity was calculated using Darcy’s Law for each site that provided hydraulic conductivity and gradient data. The correlation of the

maximum CVOC plume length per site was then compared with the corresponding mean groundwater velocity, or range of velocities, by correlation analysis.

Biogeochemical variable (i.e., independent site variable). This refers specifically to the indications of reductive dehalogenation at a given site and is treated categorically rather than in a continuous manner. Most variables are assumed to be *continuous*; their values are reported as real numbers on a continuous scale of measurement. The average for each of the independent site variables is calculated and used as a representative measure for each site in the data analyses. Ideally, mean CVOC biotransformation rates would be quantified as a continuous variable at sites where reductive dehalogenation is occurring. Statistical analyses of potential relationships between the mean biotransformation rate and plume length could then be conducted. However, given the limited spatial and temporal data available from many of the sites in the study, the systematic quantification of biotransformation rates at most of the sites was considered unfeasible. Therefore, reductive dehalogenation was treated as a *categorical* variable. A categorical variable is then represented by an integer value for each specific category.

Assignment of one of three reductive dehalogenation categories was made to all CVOC plumes at a given site. The three categories were: strong, weak, or no reductive dehalogenation potential. The categorical assignments were based upon the presence of the likely daughter products of the chloroethene reductive dehalogenation sequence, *cis*-1,2-DCE and vinyl chloride. Groundwater geochemical data from the sites were used to check the validity of the category assignments (see Appendix A, Section A-2.1.1, Site Categorization). Populations of plume lengths of CVOCs from different categories of sites were then compared to assess the effects of transformations on plume length.

CVOC physiochemical variables. These include specific properties of individual CVOCs, such as the organic carbon partitioning coefficient, Henry's Law constant, solubility, and vapor pressure that may indicate a relationship to plume behavior or CVOC concentrations. The plume lengths and maximum concentrations of individual CVOC species were compared to specific CVOC organic carbon partitioning coefficient, Henry's Law constant, solubility, and vapor pressures using correlation analysis.

## **2.3. Historical CVOC Case Data Collection**

### **2.3.1. Site Selection Process**

The purpose of the data collection and management process was to collect enough plume data in sufficient detail to test hypotheses regarding plume behavior. This included collecting information on a broad spectrum of site-specific variables that may influence plume behavior. To focus on the hypotheses of the study, the scope covered by this research excluded the following scenarios when they could be readily identified:

- Plumes that daylight substantially into surface water.
- Plumes dominated by any pumping and treating operation.
- Plumes where interpretation of plume length was complicated by multiple sources.
- Plumes with grossly indeterminate shape.

All other plumes were assumed to comprise a sufficient set from which the typical and general behaviors of CVOC plumes could be identified, while minimizing the influence of less common and more complex circumstances. Many CVOC plumes have had primary source removal either by actual physical removal of a leaking container or excavation of a disposal area or by hydraulic control of the secondary source area, without necessarily exercising hydraulic control on the distal portion of the plume. These sites were not excluded from the study.

The plume data gathering progressed in several steps (Fig. 2-1). First, partner organizations in the CVOC Initiative attempted to identify available plumes for analysis by completing a Plume Screening Checklist for candidate sites. This checklist was intended to identify which sites had a sufficient data set available for a plume to be considered by the Data Collection Team for inclusion in the historical case analysis. The CVOC Plume Screening Checklist is presented in Appendix D. Typically, the participant organization could find the information needed to complete the Plume Screening Checklist in the site Record of Decision (ROD), Remedial Investigation (RI), annual monitoring, or other similar reports.

Next, a plume screening process that identified plumes with a minimum data requirement was implemented. Plumes that passed this minimum criterion became candidates for further selection by the Data Collection Team. The key CVOC plume screening criterion was the availability of data from at least six monitoring wells sampled over at least three sampling intervals conducted over at least two years prior to the initiation of hydraulic control activities. Thus, no further screening evaluation was needed for a given plume if a participant organization case worker could not answer “yes” to this criterion. The Data Collection Team then decided which nominated sites were to be put into the Statistical Analysis of VOCs in the Environment (SAVE) database. See Figure 2-2 for the basic SAVE database structure and Appendix E for further details.

For legal and practical reasons, site names were not used in any reports issued pursuant to this study. Instead, generic site sequence numbers were assigned to each site for identification purposes. However, the site names are included in the database maintained by LLNL. Access to this database is allowed only with permission of LLNL.

Since the purpose of this study is to evaluate relationships between plume characteristics and site variables, identifying such relationships does not necessarily depend on having an ideally representative sample population so long as the sample population exhibits a broad range of plume characteristics and site variables. Such variability is well represented in the database; site historical and hydrogeological conditions for each CVOC plume analyzed are presented in Appendix F. Potential biases that may be in a data set gathered in this manner will be considered in the discussion of the study results.

### **2.3.2. Data Collection Process**

LLNL Staff or CVOC Data Collection Team representatives called and discussed the data needs with the site responsible party and their consultant and ascertained what information could be obtained in electronic format or copied from reports. Once the electronic data were received, the CVOC Data Collection Team contacted state case managers and if possible, site consultants, to discuss site characteristics and specific data gaps, and to obtain data not available electronically. Documents were then either copied by the data contributor or borrowed for

copying at LLNL. Electronic data were reformatted before being finalized in the SAVE database. Data entered into the SAVE database were queried and used as a basis to conduct the statistical analyses.

### **2.3.3. Distribution of CVOC Site Data**

An initial data collection goal of the study was to include data from up to 400 sites nationwide. For several reasons, this goal proved to be unattainable within the time frame allotted for the present data collection efforts. These reasons include:

1. Many sites did not meet our screening criteria.
2. Electronic data were not available or not accessible.
3. Legal concerns by the responsible party.
4. A lack of good quality data.
5. Uncooperative responsible parties were.
6. Difficulty in making contact with the individual who had authority to release and provide historical case data.

While over 188 screening checklists were received, only 110 were accepted as representing usable sites. Among these, a site with a usable checklist was sometimes dropped because not all of the data needed to adequately define the plume were received. While the military and governmental sites added to the geographic diversity of the data set, requests for data from state agencies and environmental consulting firms proved to be most productive in the western states of California and Oregon.

A total of 65 sites were selected as the core data set for the analyses of this study. These represent a distillation of the 188 sites that expressed an interest in participating in the study as indicated in the screening checklists. Sites beyond the original 65 sites that had subsequently supplied data for the project were used for validation analyses.

CVOC plume lengths were identified for each CVOC at each site based on the plume length algorithm discussed in Appendix B. Among the 65 sites, 247 individual CVOC plumes, including parent CVOC and daughter product plumes, as defined by a plume length practical limit estimation of 10 ppb, were identified. In addition, subsets of 134 plumes defined by the 100-ppb contour and 58 plumes defined by the 1000-ppb contour were also identified. Fewer 100-ppb and 1000-ppb plumes were delineated because the low CVOC concentrations at many of the sites.

Fig. 2-1 SAVE Database Structure : Statistical Analysis of VOCs in the Environment

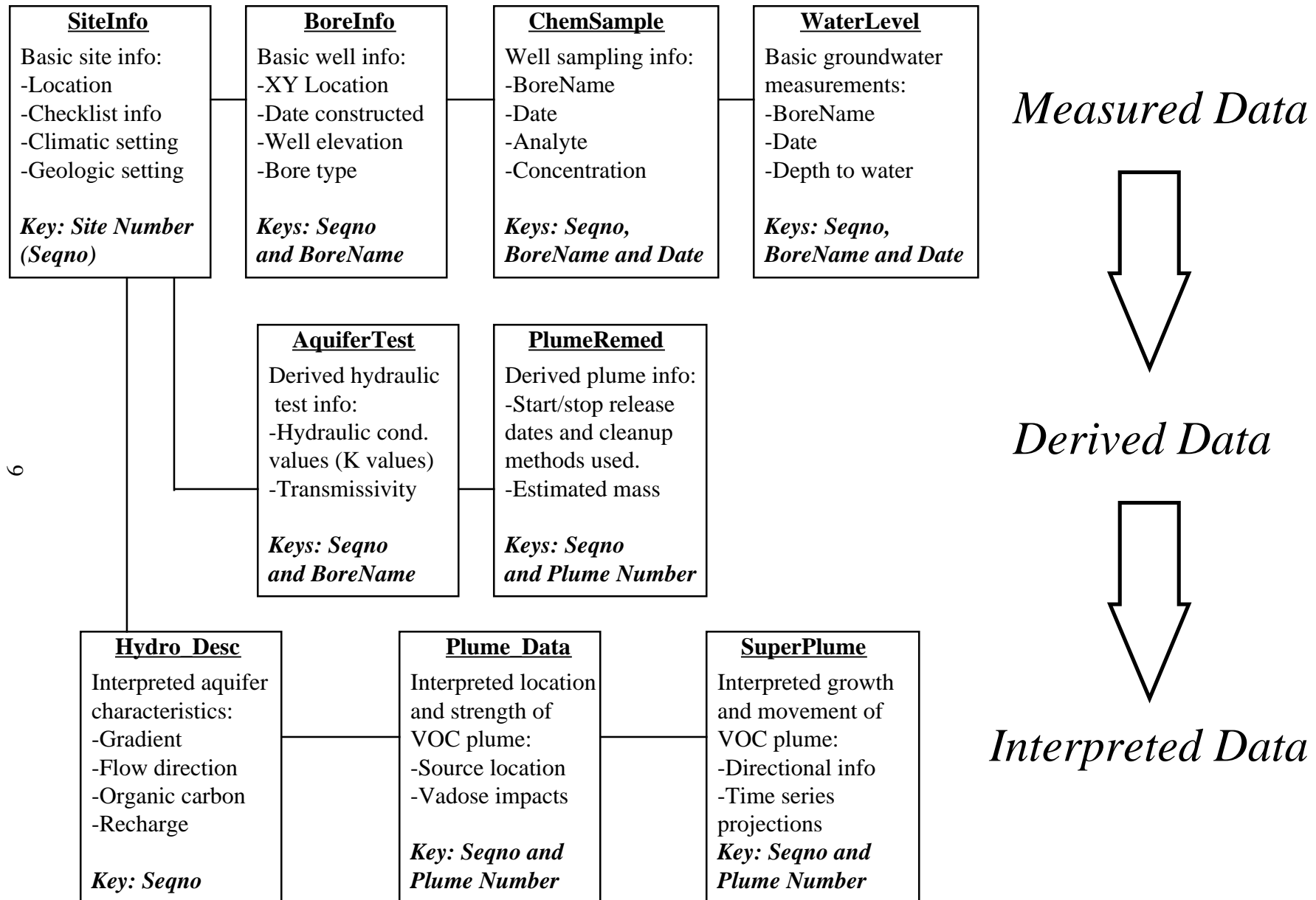
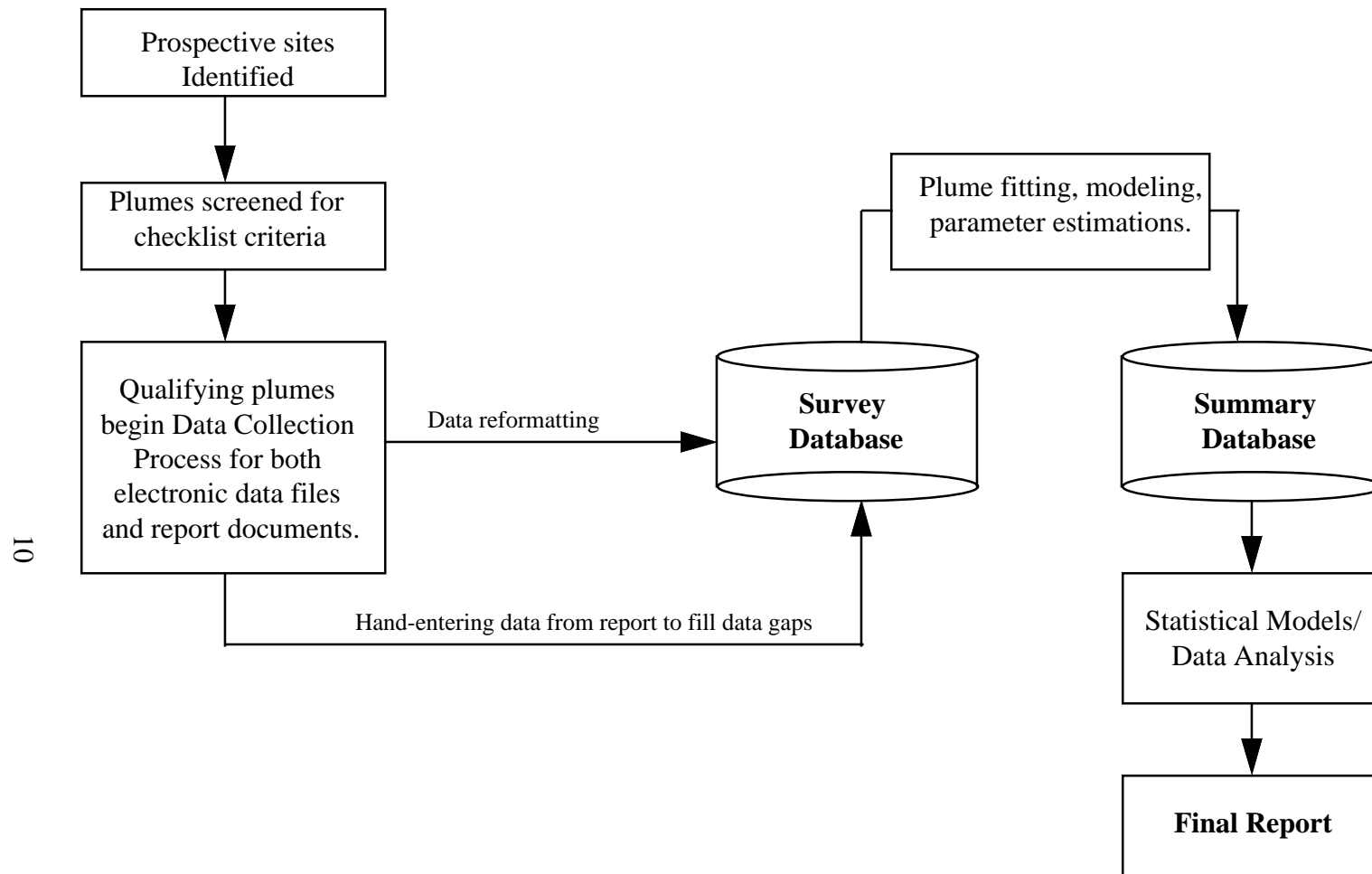


Fig. 2-2 Data collection process for adding data to the SAVE Database.



### 3. Overview of Findings

#### 3.1. General Characteristics of the CVOC Historical Case Data Set

Among all of the CVOC plumes included in this study that were defined by the 10-ppb contour, 90% of the plume lengths evaluated do not currently extend beyond approximately 6300 ft downgradient of the area of maximum CVOC concentration. This is not to imply that all CVOC plumes will be shorter than 6300 ft. Ten percent of the plumes in the CVOC historical data set were longer and some were much longer.

The number of 10-ppb plumes distributed among the 16 different types of CVOCs that were encountered in the database is shown in Table 3-1. TCE constitutes the largest population of 10-ppb plumes (55 plumes). This is followed by PCE (32 plumes), with four other CVOCs (1,1-DCE, *cis*-1,2-DCE, 1,1,1-TCA, and vinyl chloride) each yielding at least 20 plumes, and 1,1-DCA providing 18 plumes. The remaining 41 plumes are distributed among a variety of other chlorinated hydrocarbons.

The sites included in the database, to date are, distributed across the country with the largest number of sites (40) located in states in the West Coast States (Fig. 3-1). Even though the distribution of sites is heavily weighted toward the West Coast, an enormous variability among CVOC historical case data set plumes exists. For example, the relationship between plume length and reported maximum concentration for 55 TCE plumes is shown on Figure 3-2, with several non-TCE plumes included to represent all 65 sites. From Figure 3-2, it is apparent that plume lengths and reported maximum concentrations from West Coast sites are evenly scattered within the entire distribution of plume lengths and reported maximum concentrations observed in the data set.

The degree of characterization of the CVOC sites in the data set is difficult to assess, but the number of monitoring wells may be used as a crude measure of the level of site characterization. The distribution of the number of monitoring wells per site with respect to four broad types of sites used for data, namely (1) Department of Defense (DOD), (2) Department of Energy (DOE), (3) industrial (including dry cleaning, grain storage, semiconductor manufacturing, and others), and (4) landfill, is shown on Figure 3-3. In the present data set, there are 15 DOD sites, 18 DOE sites, 28 industrial sites, and four landfills. The industrial sites are generally characterized by fewer wells than the DOD or DOE sites. Ninety percent of the industrial sites have 40 or fewer monitoring wells, compared to 50% of the DOD sites and 40% of the DOE sites. The number of monitoring wells at the DOD and DOE sites is more evenly distributed over the categories shown on Figure 3-3. The only sites with 100 or more monitoring wells are either DOD or DOE sites.

The number of monitoring wells per site does not correlate well with either plume length or maximum historical TCE concentration (Fig. 3-4). Of the 25 TCE plumes longer than 1000 ft shown on Figure 3-4, four were characterized by fewer than ten wells, and 10 others by between 11 and 50 wells. The relatively small number of wells used to characterize long plumes in some cases raises the question of how well those plumes have been characterized. Also worth noting

is that the three longest TCE plumes span three orders of magnitude in maximum concentration, and the three shortest plumes, two orders of magnitude. Conversely, over each order of magnitude in the maximum historical TCE concentrations shown, the spread in plume length is two orders of magnitude or less.

The range of plume length and reported maximum concentration for the TCE plumes is shown by site type in Figure 3-5. Plumes from DOD, DOE, and industrial sites span over four orders of magnitude in terms of the reported maximum concentration of TCE. The range of plume length is slightly larger for DOD (over two orders of magnitude) and DOE (over one order of magnitude) sites compared to industrial sites. DOD and DOE sites have both the longest and the shortest plume lengths of all TCE sites in the data set.

### **3.2. Summary of CVOC Plume Characteristics**

The longest (maximum) CVOC plume length at each site, irrespective of the type of CVOC measured, may be used to develop conservative site plume length frequency distributions. The distributions, which are approximately lognormal in nature, are shown on Table 3-2 for the 10-, 100-, and 1000-ppb-defined plumes. In general, 10-ppb plumes are typically on the order of 20% longer than 100-ppb plumes at most sites, whereas the 100-ppb plumes are on the order of 50% longer than the 1000-ppb plumes where the three coexist. Among the individual CVOCs represented in the data set, two observations emerge from summary statistical analyses:

1. Plume lengths defined by the 10-ppb isocontour are approximately lognormally distributed, although with some deviations. For example, an inference test of normality (Shapiro-Wilk *W*-Test) on the log-transformed plume length data indicates a statistically significant departure from an assumption of normality in the log distributions of plume lengths. In particular, short plume lengths appear to be under-represented and shorter than expected in this data set based on a log-normal probability distribution model. These findings are explored further in Appendix C.
2. There are no statistically significant differences in log-transformed 10-ppb plume length populations between the various CVOCs represented, based on an analysis of variance, or ANOVA (refer to Appendix C). This finding is important for a number of reasons. Use of the entire plume data set for certain correlation analyses would require that there are no significant differences between plume length populations among different CVOCs. From a process-oriented perspective, the lack of statistically significant differences in plume lengths between CVOCs holds important implications for the relationship between parent contaminants and transformation daughter product species. For example, a statistical equivalence in plume lengths between parent and daughter CVOCs may imply that the daughter product plumes are affected by attenuation processes (e.g., subsequent transformations, dispersion, volatilization). If daughter products are not attenuated in some manner, then the accumulation of daughter product mass would eventually yield significantly longer daughter product plumes. Alternatively, this finding may suggest that variability in physical transport variables such as the rate of advection may influence plume behavior more strongly than biogeochemical variables.

For 141 of the 247 plumes defined by the 10-ppb contour, a sufficient monitoring history existed to permit estimation of plume growth rates for comparative purposes. This corresponds



to at least one CVOC plume from 48 of the 65 sites studied. Rank correlation analysis, with the rank of the annually averaged plume length as the dependent variable and the rank of the monitoring year as the independent variable, was used to quantify the proportion of plumes undergoing growth, shrinkage, or exhibiting no significant trend (See Appendix A, Section A-2.1.4). The median time period used for evaluating plume growth was six years, with a range between three and 15 years. Among plumes from sites exhibiting strong evidence of reductive dehalogenation, roughly equal numbers of plumes appeared to be undergoing either a significant increase or decrease in length with time. In contrast, among plumes from sites lacking strong evidence of reductive dehalogenation, approximately twice as many plumes appeared to be increasing in length as opposed to exhibiting a decline.

### **3.3. Correlation of Plume Behavior with Hydrogeologic and Chemical Variables: A Summary**

Analyses of the data collected in this study have shown statistically significant trends involving certain aspects of CVOC plume behavior and all of the independent variables discussed in Section 2.2, e.g., source strength, groundwater velocity, and biotic and abiotic transformations. The relationships between plume length and the variables related to the physics of contaminant transport, namely the roles of the source term and groundwater velocity, are the strongest. For example, a statistically significant correlation is observed between plume length and maximum concentration, with the correlation improving when higher concentration contours were used to define plume length (i.e., 100-ppb and 1000-ppb defined plumes). This finding may reflect the increasing proximity to the source area, where variability in maximum concentration would be expected to have a stronger relationship to the variability in plume length.

Reported maximum concentrations for individual CVOCs have been used by some workers as evidence for the presence of an active DNAPL source based on certain established rules-of-thumb, such as 1% or 10% of the solubility limit (Newell and Ross, 1991; and Feenstra and Cherry, 1988, respectively). Table 3-3 summarizes the fraction of plumes where reported maximum concentrations greater than the 1% and 10% solubility limits were observed for CVOCs represented by more than 10 plumes in the data set. Approximately 40% of the TCE plumes may be associated with DNAPL based on a 1% solubility limit rule-of-thumb and approximately 10% of the TCE plumes may be associated with a DNAPL based on a 10% rule-of-thumb.

The results of this study suggest that, in general, a high maximum CVOC concentration at a given site is often associated with a relatively long plume. This is especially true when plume length is defined with reference to higher concentration contour thresholds (e.g., 100- or 1000-ppb plumes). When these higher concentrations are used to define plume lengths, the proportion of plumes that are potentially associated with DNAPL increases. In particular, based on 1% and 10% solubility limit rules-of-thumb, maximum concentrations suggest the presence of DNAPL in a majority of cases where a 1000-ppb TCE plume may be defined. See Appendix A.

Plume length also correlates with the groundwater velocities estimated for sites in the data set (See Appendix A). In general, CVOC plume lengths appear to be much better correlated with different CVOCs at the same site than with the same CVOC across multiple sites. For example,

the median ratio of the longest plume length to the shortest plume length among CVOCs at individual sites is approximately 3.3; whereas the median ratio of longest plume length to shortest plume length for individual CVOCs across multiple sites (for CVOC species represented by at least 6 plumes) is approximately 140. This analysis, aside from the other statistical tests, also suggests that site physical conditions are much more important in determining plume length than biogeochemical and physiochemical properties of the individual compounds.

In contrast to readily apparent relationships observed with the physical contaminant transport variables, clear relationships between CVOC transformation process categories or physiochemical variables and plume length are not apparent upon first inspection. For example, a plume's reductive dehalogenation category appears to have little relationship to plume length variability in comparison to other factors such as source strength or groundwater velocity. However, when the effects of these site variables are factored out using an indexing scheme or multivariate statistical analysis, a significant relationship between reductive dehalogenation categories and plume length becomes apparent.

Based on the presence or absence of *cis*-1,2-DCE and vinyl chloride reductive dehalogenation daughter products, the CVOC sites sampled in this study are divided roughly into equal thirds in terms of no evidence of reductive dehalogenation (no *cis*-1,2-DCE or vinyl chloride plumes), weak evidence of reductive dehalogenation (*cis*-1,2-DCE plumes but no vinyl chloride plumes), and strong evidence of reductive dehalogenation (vinyl chloride plumes present) (See Appendix A, Section A-2.1.1). Analyses of plume lengths from these three groups suggests that CVOC plumes are significantly shorter at sites where a vinyl chloride plume exists compared to plumes from other sites, after the effects of other variables such as source strength and groundwater velocity are factored out.

There is also some evidence to indicate that CVOC plumes at sites characterized by vinyl chloride plumes may exhibit lower growth rates. In contrast, the presence of a *cis*-1,2-DCE plume in the absence of a vinyl chloride plume indicates reductive dehalogenation rates that are insufficient to effectively reduce the extent of CVOC plumes; little evidence exists to suggest that plume lengths and plume growth rates are substantially affected by reductive dehalogenation in these circumstances. This finding is consistent with a survey of geochemical indicator species at these sites. In contrast to sites with vinyl chloride plumes, sites with only *cis*-1,2-DCE plumes present much less convincing evidence that fuel hydrocarbon oxidation is driving the biogeochemical setting toward a significant reductive dehalogenation environment.

A statistical evaluation of spatial relationships between daughter product and parent product plumes is not a straightforward process. During this study, plume lengths were defined for each CVOC with respect to the location of maximum historical concentration of that particular CVOC. This process of defining plumes was applied consistently to all CVOCs at all sites within the study because the precise source area or source area(s) were often unknown or unspecified. Given the spatial and temporal variability associated with CVOC plumes, and the sensitivity of inferred plume morphology to monitoring well locations, we concluded that measuring daughter product plume lengths with respect to the location of maximum concentration of the suspected parent product could not be justified *a priori*. Therefore, indirect methods of analysis were required in the context of this study to assess spatial relationships between daughter and parent product plumes (See Appendix A, Section A-2.1.3 and Appendix B for an expanded presentation of these methods and findings).

With regard to the spatial relationships between parent and daughter product CVOC plumes, it appears that, in general, daughter plumes do not typically extend much farther downgradient than the parent product plumes. In summary, evidence to support this conclusion includes:

1. There appears to be a lack of significant differences in plume length distributions between parent and daughter compounds (e.g., vinyl chloride plume lengths are not systematically longer than TCE plume lengths) (Appendix C, Fig. C-1).
2. Parent product compounds (e.g., PCE, TCE) form longer plumes than the probable daughter product compounds (e.g., *cis*-1,2-DCE, vinyl chloride) in the majority (73%) of the cases observed (Table 3-4).
3. The separation between parent and daughter product maximum concentration locations within co-mingled plumes is usually not large compared to the maximum plume length at the given site. Plume lengths are measured with reference to the location at which the reported maximum concentration was measured (i.e., the presumed source area). Among likely parent-daughter compound combinations (e.g., TCE and *cis*-1,2-DCE, *cis*-1,2-DCE and vinyl chloride), the distances between the respective maximum concentration locations are on the order of 10% to 25% of the maximum plume length at most sites.

Among the CVOC physiochemical and source strength variables, significant correlations appear to exist between the variability in maximum concentration between sites and both the organic carbon partitioning coefficient and the Henry's constant. In addition, there is a possible correlation between plume length and the Henry's constant, once factors such as source strength and groundwater velocity are accounted for through the plume length index. Although these relationships are statistically significant and are consistent with idealized conceptualizations of plume behavior, these results must be viewed as preliminary in nature; further studies should be conducted to independently confirm these observations.

All of these findings are discussed in detail in Appendix A.

**Table 3-1. Summary of the number of different types of CVOC plumes that were recognized in the historical case data set using a range of isoconcentration contours.**

CVOC	10-ppb plumes (from 65 sites)	100-ppb plumes (from 55 sites)	1000-ppb plumes (from 30 sites)
TCE	55	37	19
PCE	32	20	8
1,1-DCE	29	17	8
<i>cis</i> -1,2-DCE	29	17	7
1,1,1-TCA	23	16	9
Vinyl chloride	20	10	4
1,1-DCA	18	10	2
Chloroform	8	1	0
<i>trans</i> -1,2-DCE	8	0	0
Carbon tetrachloride	7	2	1
1,1,2-TCA	6	0	0
1,2-DCA	6	2	0
Chloroethane	2	1	0
Chloromethane	2	0	0
Methylene chloride	1	1	0
1,1,2,2-TCA	1	0	0
<b>TOTAL</b>	<b>247</b>	<b>134</b>	<b>58</b>

**Table 3-2. Summary of frequency distributions of maximum CVOC plume lengths (ft) per site, based on the indicated concentration contour definition.**

Quantile	10-ppb-defined plumes	100-ppb-defined plumes	1000-ppb-defined plumes
10 <sup>th</sup>	420	250	90
25 <sup>th</sup>	790	500	230
50 <sup>th</sup>	1600	1100	650
75 <sup>th</sup>	3210	2400	1830
90 <sup>th</sup>	6030	4840	4630

**Table 3-3. Fraction of plumes possibly associated with DNAPL for CVOCs represented by more than 10 plumes in the historical case analysis data set.**

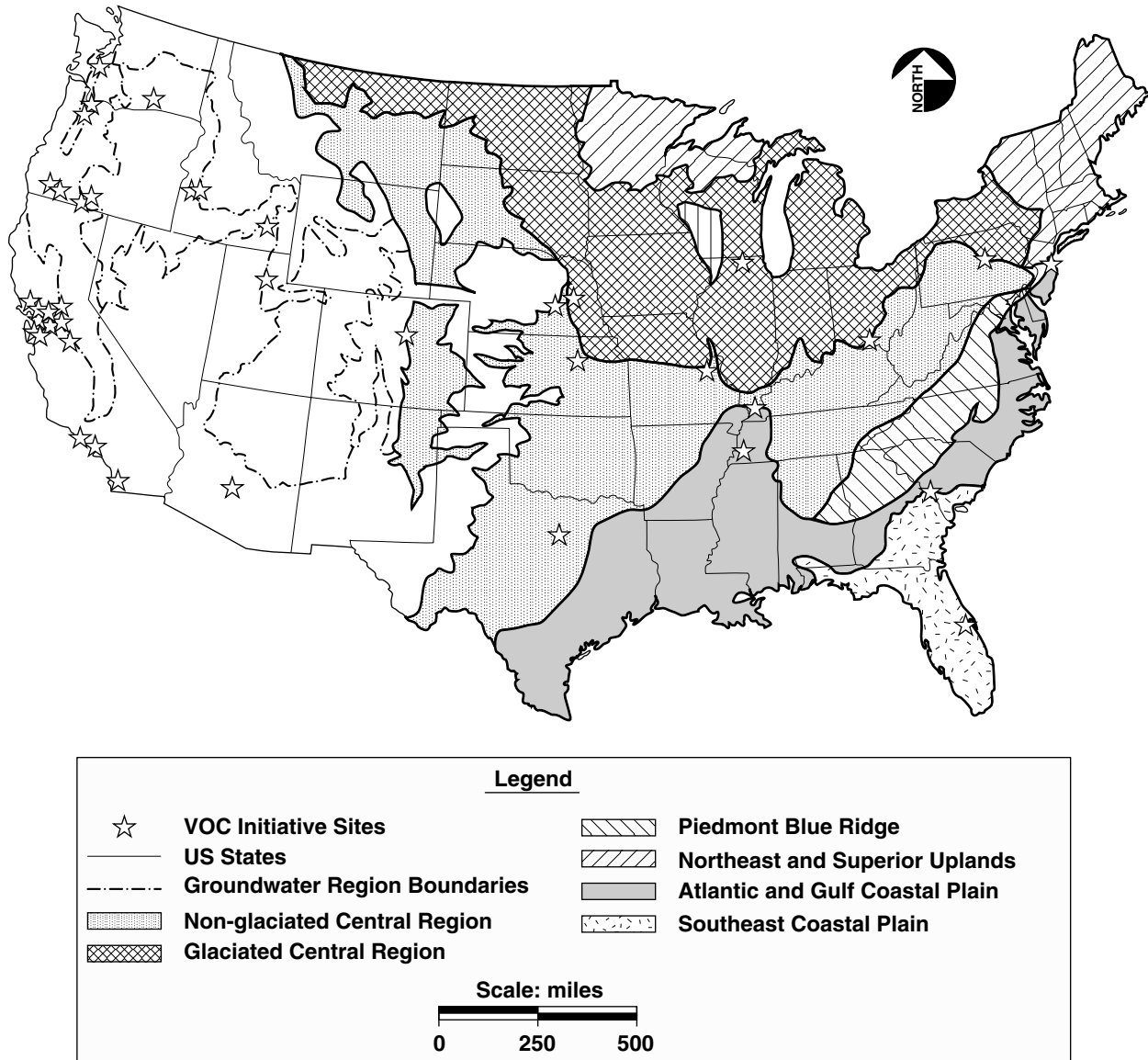
CVOC	Total number 10-ppb-defined plumes	Fraction plumes with conc. > 1% solubility	Fraction plumes with conc. > 10% solubility
TCE	55	36% (20 plumes)	11% (6 plumes)
PCE	32	38% (12 plumes)	13% (4 plumes)
1,1-DCE	29	10% (3 plumes)	0%
<i>cis</i> -1,2-DCE	29	7% (2 plumes)	3% (1 plume)
1,1,1-TCA	23	26% (6 plumes)	4% (1 plume)
Vinyl chloride	20	0%	0%
1,1-DCA	18	0%	0%

Note:

conc. = Concentrations.

**Table 3-4. Comparison of TCE parent plume length and reductive dehalogenation sequence daughter product plume length.**

Parent/daughter pair	Number of sites with pair	Parent plume is longer	Daughter plume is longer
TCE/ <i>cis</i> -1,2-DCE	24	18	6
TCE/vinyl chloride	17	13	4
<i>cis</i> -1,2-DCE/vinyl chloride	10	6	4
<b>TOTAL</b>	<b>51</b>	<b>37 (73%)</b>	<b>14 (27%)</b>



States	Number of Sites	States	Number of Sites
California	27	Florida	1
Oregon	10	Illinois	1
Ohio	4	Kansas	1
South Carolina	4	Kentucky	1
Idaho	3	Missouri	1
Washington	3	New Jersey	1
Nebraska	2	Tennessee	1
Pennsylvania	2	Texas	1
Arizona	1	Utah	1

From: S. Belding, 6/29/98

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Figure 3-1. Distribution of VOC study sites in Heath's groundwater regions.

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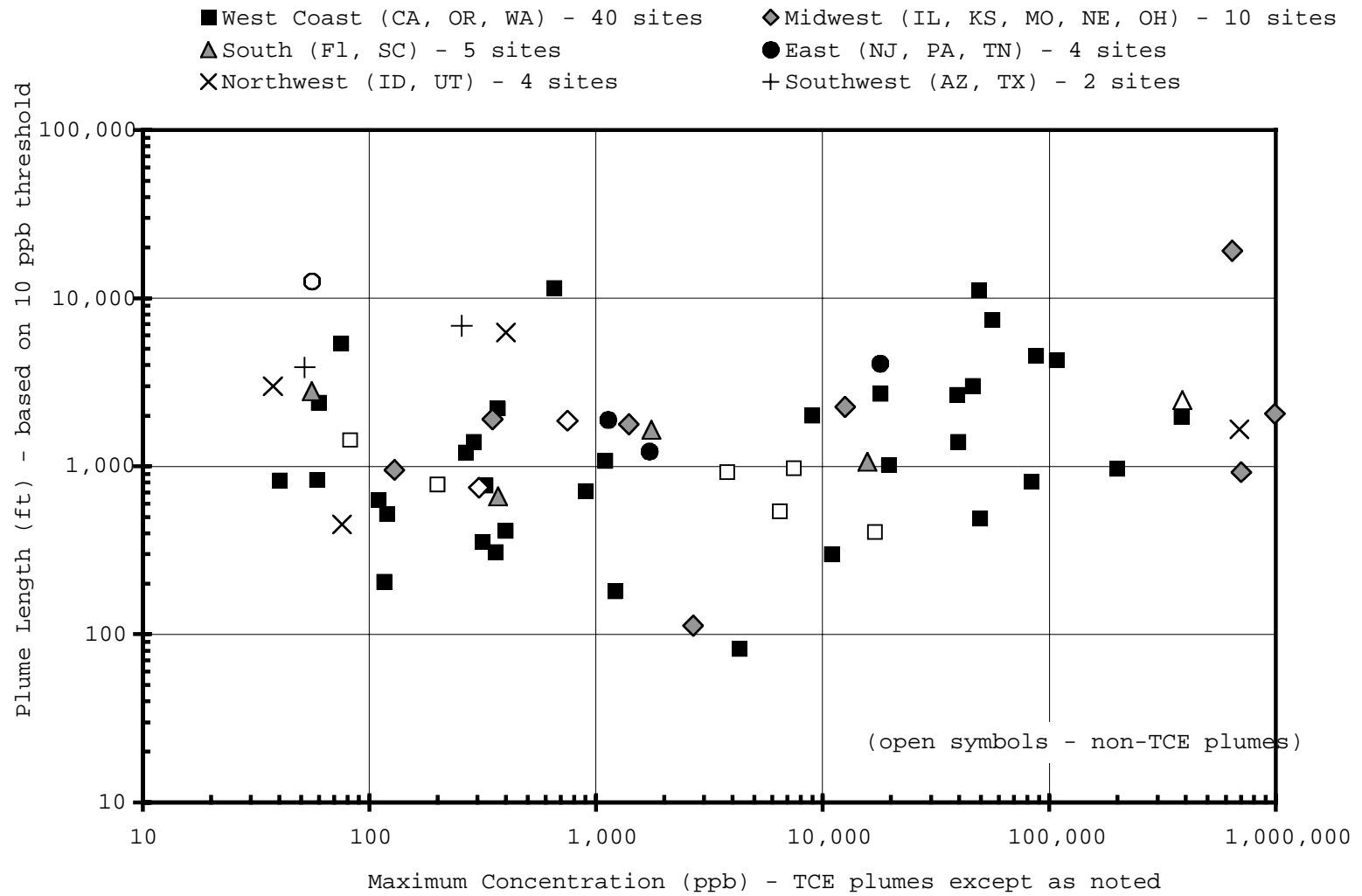


Figure 3-2. Distribution of 10-ppb-defined TCE plumes in terms of plume length and maximum concentration, delineated by region.

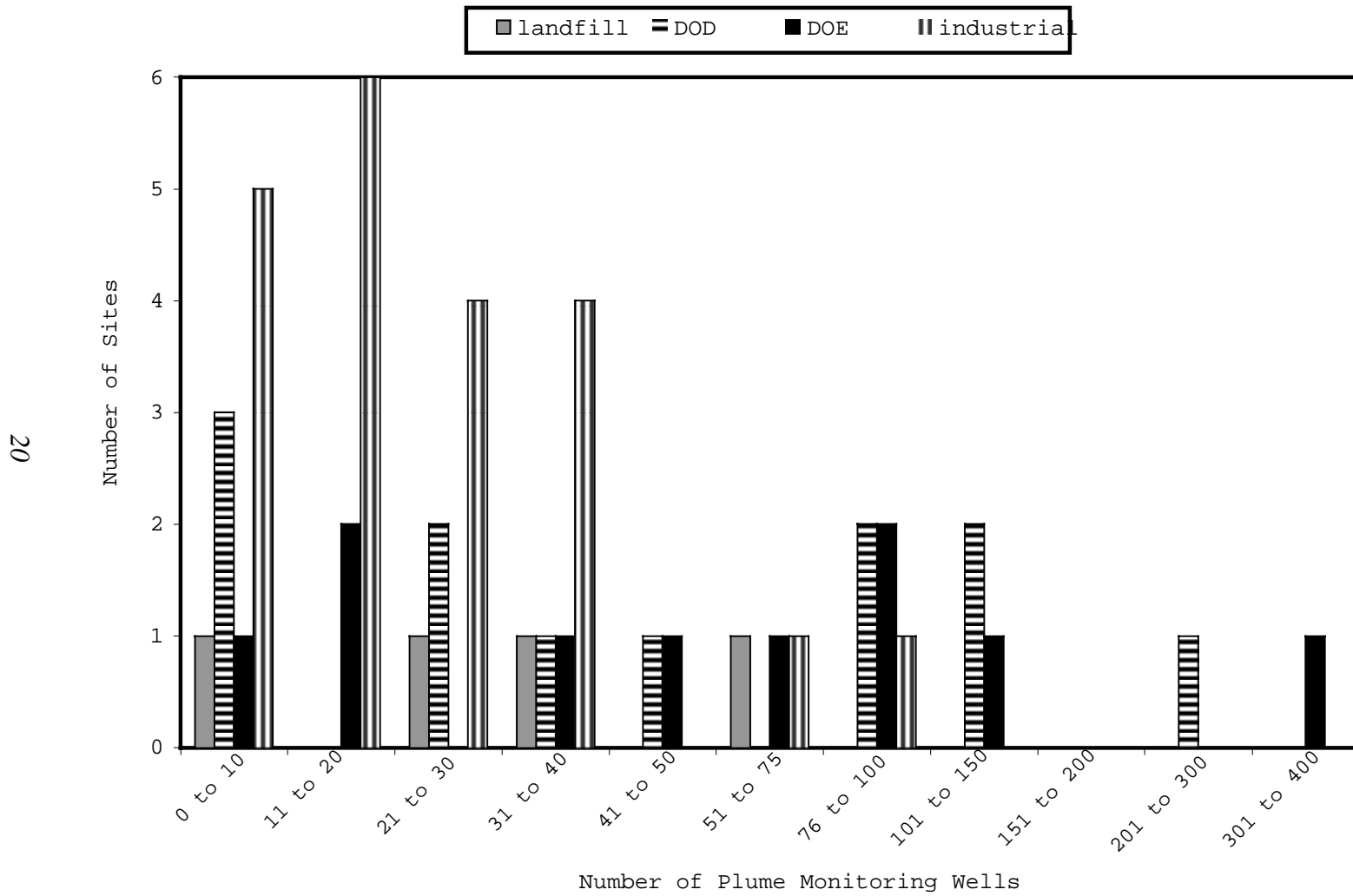


Figure 3-3. Distribution of number of plume monitoring wells by type of site (DOD, DOE, industrial, or landfill).



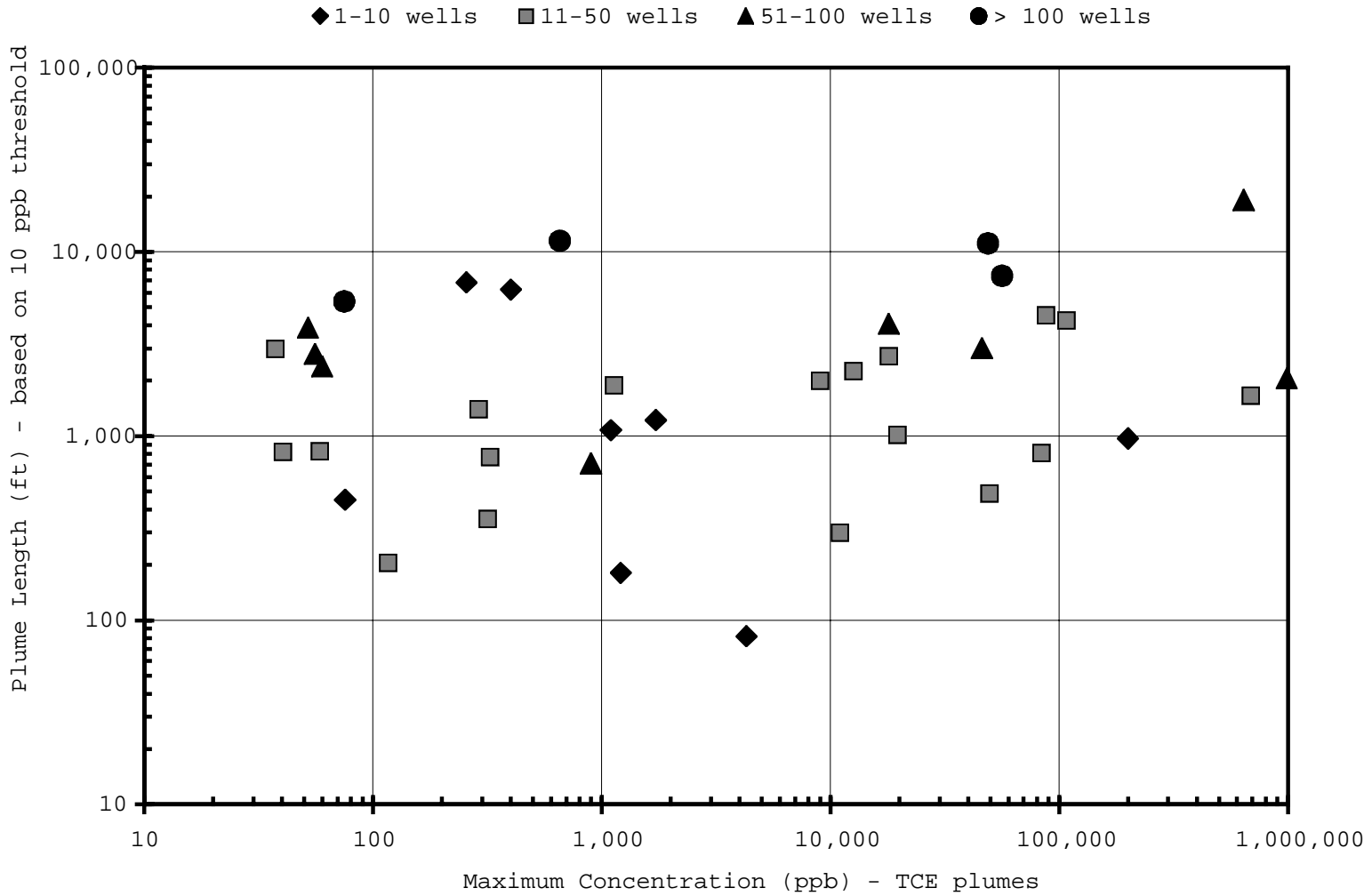


Figure 3-4. Distribution of 10-ppb-defined TCE plumes in terms of plume length and maximum concentration, delineated by number of monitoring wells per site.

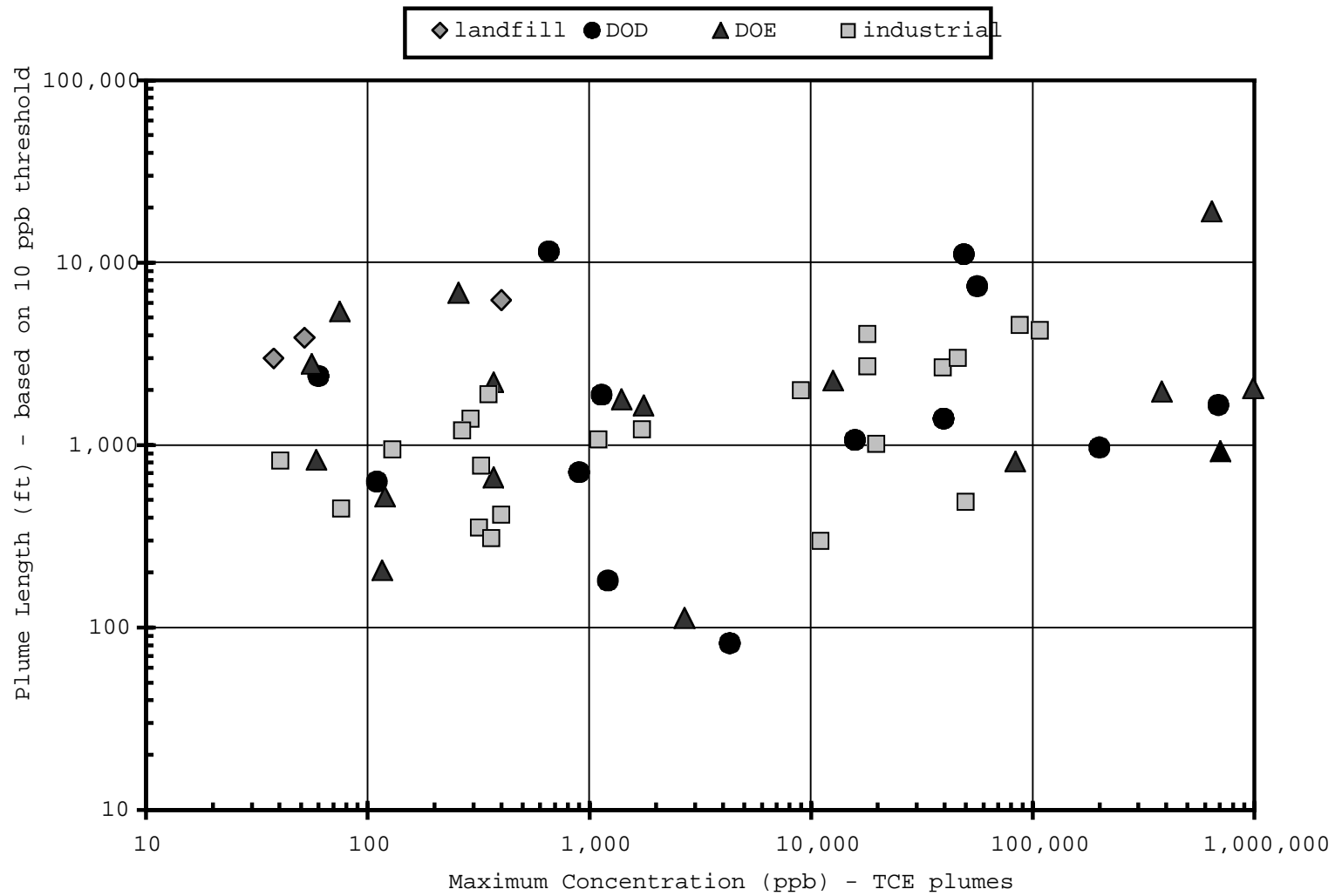


Figure 3-5. Distribution of 10-ppb-defined TCE plumes in terms of plume length and maximum concentration, delineated by type of site.

## 4. Conclusions

This study provides the first statistical analysis of data from a relatively large population of CVOC plumes and has demonstrated that broad trends in relationships between plume behavior and key site variables can be determined through the statistical analyses of field data from a large number of sites. This finding is important because it demonstrates that:

1. Specific hydrogeologic conditions and contaminant release scenarios at individual sites are not so unique that expected overall trends in the data are completely obscured.
2. Useful average values for site variables such as hydraulic conductivity and groundwater velocity can be quantified in most situations.

This study also shows that statistical methods, such as general linear models and comparison of probability distributions of plume length indices, are useful in quantifying expected relationships between plume length and site variables and CVOC variables within a population of CVOC plumes. In addition, it provides population statistics that may be used to bound the uncertainty inherent in these expected plume behaviors.

The study provides quantitative confirmation that plume behaviors can be grouped and that these groupings are based on expected hydrogeologic processes. An important conclusion of the groupings used in this study is that the presence of *cis*-1,2 DCE without the presence of vinyl chloride may indicate that reductive dehalogenation rates may be insufficient to effectively reduce the extent of CVOC plumes. Another important conclusion is that CVOC transformation rates through dehalogenation have less impact on plume length than source strength and groundwater velocity. Thus, plumes with lower source strength and groundwater velocities may be better candidates for the application of natural attenuation remedies.

### 4.1. Can Historical Case Data Be Used to Predict CVOC Plume Behavior?

One of the major features of this study is that its analyses and conclusions are based primarily on actual field observations, i.e., data from actual CVOC plume historical cases. At present, there is no evidence that the historical case data can be used predictively outside the range of data reviewed. The strength of the conclusions arising from statistical analyses of the CVOC data are dependent upon data set characteristics, particularly the representativeness and the quality of the data. It must be noted that the plume length distributions, relative plume growth rates, and the types of CVOCs involved are reflective of the 65 sites in the project database, exclusively. There is no way of ascertaining whether or not these distributions present an unbiased sample of the entire population of CVOC plumes across the U.S. without conducting a much larger survey on a vast scale. As more data are added to the CVOC historical data set, representativeness will be enhanced.

On a purely conceptual level, the findings that significant observable relationships between plume length and variables are related to the physics of transport may appear intuitive and obvious. However, it is important to recognize that one of the central issues in conducting historical case analyses of multi-site data is whether or not any common trends may be discerned

through the statistical noise created by the specific circumstances associated with individual sites. The significant correlations noted in the data indicate that this is indeed possible. This finding is therefore essential for providing credibility to the other results developed in the study and demonstrating the usefulness of using historical case analysis.

The value of the historical case analysis conclusions for predicting future CVOC plume behavior at a given site must be weighed against known uncertainties in the data and future events. The analysis results represent a retrospective view of a population of CVOC plumes characterized over a relatively short time period. For example, we often do not know over what period of time reductive dechlorination has occurred or may continue to occur at sites, so the long-term or future expectation for reductive dechlorination to occur at a given site is not predictable based on historical data alone.

To use the historical case analysis results to forecast the likelihood of behaviors in future CVOC plume populations requires a link to mechanisms. Since many of the relationships observed in the data are the result of correlation analysis, direct links to cause and effect are not established. The link to mechanisms is established through the use of probabilistic modeling which incorporates the mechanisms of CVOC plume fate and transport. The agreement between probabilistic modeling results and observed plume characteristics enhances the credibility of the data set and the analysis procedures. Furthermore, as new data from existing plumes are added with time, the comparison of new data to the existing historical data will provide direct evidence of the utility of historical case analysis in predicting plume behavior.

#### **4.2. What are Key Uncertainties Associated With Evaluating CVOC Plume Behavior Using Historical Case Data and What Other Types of Data are Needed?**

The specific findings, while intuitively reasonable, must be considered preliminary in nature because the modest size of the data set does not statistically capture all of the variability anticipated to exist across CVOC sites with reference to hydrogeology, climate, release scenario, etc. Also, the strength of the conclusions should be tempered by the knowledge that some sites have long plumes and relatively few monitoring wells, which leads to questions about the level of characterization.

Further, it is conceivable that the data used for this historical case analysis may reflect a bias created by the screening checklist criteria. For example, very long plumes may not be included in the data set since pump-and-treat remediation systems may have been installed at such sites early in the site investigation history. Such plumes are also more likely to daylight into surface waters. Small plumes may not be represented sufficiently in the data set; such plumes may not be characterized by a monitoring well network of sufficient size to meet minimum acceptance criterion.

These general limitations are compounded by the incomplete nature of the data in terms of hydrogeologic variables supplied by many of the sites. A more comprehensive data set may shed light on some of the questions that could not be answered completely in this present study or else could not be addressed at all. These questions are discussed further in Section 5.

### **4.3. How May CVOC Historical Case Analysis Be Used in Cleanup Decision-Making?**

The results of this historical case analyses may be used by a site manager to develop initial site conceptual models and help focus characterization resources on data that will be most useful in confirming or denying conceptual model hypotheses. For example, a site manager can measure the length of a CVOC plume to the 10-ppb contour, use maximum groundwater concentrations from a well near the CVOC release area and the mean groundwater velocity to calculate a site-specific plume length index. As explained in Appendix H, the plume length index, calculated by dividing the plume length by the product of the reported maximum concentration and the groundwater velocity, provides a means by which plumes may be compared to one another. Plumes exhibiting strong evidence of reductive dehalogenation tend to be characterized by relatively low plume length indices in comparison to the population of plumes evaluated in this study, as a whole. This information can be used directly to help confirm or refute specific hypotheses developed by site investigators pertaining to the role of reductive dehalogenation. Examples of this approach are presented in Appendix H.

The results of the CVOC historical case analyses also may prove useful to a more general audience. Some examples include:

- The study provides information on the types of data that are not currently being collected that should be collected. For example, the contaminant chemistry was generally found to be the most complete of the types of data reviewed, but data on hydraulic conductivity and organic carbon content of soils and groundwater were less systematically collected and/or reported. Theoretically these parameters should be key to understanding the fate and transport of subsurface contaminants.
- A key practical component to applying a natural attenuation remedial alternative is providing some guarantee that funds will be available for long-term monitoring and implementation of contingency plans if the natural attenuation remedial alternative is shown to have not met expectations. This guarantee may be provided by a performance bond or an insurance policy. The historical case analyses results may provide an actuarial basis for these financial guarantees that is defined in a systematic manner.
- In addition to the scientific findings, an important product of the study was the creation of an electronic database containing hydrogeological, geochemical, and other relevant data for a number of CVOC sites. These data will be made available to other investigators who may conduct future studies.

The precedent set by this study for the utility of statistical analyses of data across a number of sites suggests that the scope of future similar endeavors may include the behavior of plumes under the influence of engineered remediation measures. For example, the effectiveness of pump-and-treat, engineered source removal, and natural attenuation as exclusive remedial measures could be compared to one another across a range of environmental and hydrogeologic settings. Such information could serve a key role in shaping site cleanup decisions by site investigators, stakeholders, and regulatory agencies.

#### **4.4. How Often is a DNAPL Inferred to be Present at Sites Within the CVOC Historical Data Set and What is the Relationship of Inferred DNAPL Presence to the Plume Length at a Given Site?**

Reported maximum concentrations for individual CVOCs have been used by other workers as evidence for the presence of an active DNAPL source based on certain established rules-of-thumb, such as 1% or 10% of the solubility limit (Newell and Ross, 1991; and Feenstra and Cherry, 1988, respectively). Based on the rules-of-thumb as indicators of free-phase CVOCs, these observations suggest that the DNAPL may be influencing plume behavior to a certain extent, although not in the case of daughter product species (e.g., *cis*-1,2-DCE, vinyl chloride, possibly 1,1-DCA and 1,1-DCE in some cases). In particular, based on 1% and 10% solubility limit rules-of-thumb, maximum concentrations suggest the presence of DNAPL in a majority of cases where a 1000-ppb TCE plume may be defined.

It must be emphasized that these inferences are based entirely on very general rules-of-thumb that have been established in the contaminant hydrology literature. In reality, there is no direct way of ascertaining whether DNAPLs are present at the sites, given the data provided for this study. However, the relationships between plume length and reported maximum concentration are likely to reflect the overall strength of the source term, which may in turn be influenced by the presence or absence of DNAPL, as well as the capacity for any residual DNAPL to be actively leached into groundwater.

#### **4.5. How Often are Transformation Processes Encountered in CVOC Plumes in the Data Set and What are the Relationships Between the Indications of Transformations and Plume Length?**

Based on the presence or absence of *cis*-1,2-DCE and vinyl chloride reductive dehalogenation daughter products, the CVOC sites sampled in this study are divided roughly into equal thirds in terms of no evidence of reductive dehalogenation (no *cis*-1,2-DCE or vinyl chloride plumes), weak evidence of reductive dehalogenation (*cis*-1,2-DCE plumes but no vinyl chloride plumes), and strong evidence of reductive dehalogenation (vinyl chloride plumes present). Analyses of plume length indices (plume lengths adjusted for source strength and groundwater velocity) from the three groups indicate that CVOC plumes exhibit shorter plume lengths at sites where a vinyl chloride plume exists compared to plumes from other sites. The conclusion may be drawn that the presence of a vinyl chloride plume indicates that reductive dehalogenation may be playing a role in reducing the extent of CVOC plumes at approximately one-third of the sites. In contrast, the presence of a *cis*-1,2-DCE plume in the absence of a vinyl chloride plume appears to indicate reductive dehalogenation rates that are insufficient to effectively reduce the extent of CVOC plumes; little evidence exists to suggest that plume lengths and plume growth rates are substantially affected by reductive dehalogenation in these circumstances.

## 4.6. Do Daughter Product Plumes Behave Differently From Parent CVOC Plumes?

Reductive dehalogenation is a sequential process in which chlorine atoms are removed from a CVOC compound, producing intermediate less-chlorinated daughter products, that may themselves be subject to further transformation(s). Thus, there is an obvious concern that daughter product plumes may develop that might migrate downgradient of the attenuating parent product plume. Indeed, if comparatively high toxicity compounds, such as vinyl chloride, develop substantial downgradient plumes as a result of reductive dehalogenation, an *increased* environmental threat could potentially result.

The analysis of the data in this study indicates that, for the most part, daughter product plumes are contained within, or roughly coincide with, the respective parent product plumes. This finding is supported by several lines of evidence:

- The distributions of logarithms of plume lengths from all sites in the data set among parent and daughter compounds (e.g., PCE, TCE, *cis*-1,2-DCE, vinyl chloride) do not differ from one another in a statistically significant manner. If parent product species such as PCE or TCE were transformed into daughter products (*cis*-1,2-DCE, vinyl chloride) at rates substantially faster than the subsequent transformations of the daughter products, then *cis*-1,2-DCE and vinyl chloride plumes would be expected to be much longer, on average, than those of PCE and TCE. This is not the case. One explanation is that *cis*-1,2-DCE and vinyl chloride can continue to undergo reductive dehalogenation to ultimately produce ethene, or may be oxidized to yield carbon dioxide, water, and chloride ions. Recent studies have shown, for example, that vinyl chloride can be oxidized by ferric iron reduction (Bradley and Chapelle, 1996).
- At specific sites with suspected parent-daughter product plume pairs (e.g., TCE/*cis*-1,2-DCE, TCE/vinyl chloride, *cis*-1,2-DCE/vinyl chloride), the parent product plume was observed to be the longer of the two plumes in the majority of cases (37 out of 51, or 73%). Again, if daughter product plumes were systematically recalcitrant in comparison to the parent product plumes, this finding would not be expected. At sites where the daughter product plumes were observed to be longer, the difference in plume lengths was generally on the order of 10%-20% greater than the parent product plume length.
- The offset in locations of observed maximum concentrations of parent and daughter product plumes was, for most plumes, generally on the order of 10%-20% of the parent product plume length, again suggesting a rough coincidence of parent-daughter plumes. However, at approximately one-third of the sites, the maximum concentration offset was greater, on the order of 50% or more of the parent product plume length. A number of explanations could account for this phenomenon, including localized reductive dehalogenation far downgradient of the parent source area, slow reductive transformation rates in comparison to groundwater velocity, or high detection limits of the daughter product in the vicinity of the parent product source area. Nevertheless, even at these sites, the combined parent product-daughter product plume length exceeded that of the parent product alone by greater than 5% in only one-third of the cases. Thus, while the apparent internal morphology of the parent and daughter plumes differed at these sites,

the plume boundaries (as defined by the 10 ppb contour) were roughly coincident in the majority of cases. Refer to Appendix A, Section A-2.1.3 for discussion.

It is important to recognize that these findings all pertain to the *average* behavior of plumes from a sampling large number of sites. At any individual site, a large vinyl chloride plume emanating from a small, attenuating TCE plume could potentially constitute a threat equal to or greater than the original TCE plume if no attenuation had occurred. Such cases must always be carefully investigated on an individual basis. This present study indicates, in a general sense only, that such a scenario is probably less common than not. Potential explanations for this general observation include: (1) subsequent natural attenuation of daughter product plumes (e.g., subsequent biotransformations, dispersion, volatilization), and (2) dominance of other factors, such as groundwater velocity, that may influence plume length.

#### **4.7. What is the Relationship of Fuel Hydrocarbon Co-contamination to CVOC Plume Behavior?**

The statistical association between fuel hydrocarbons, elevated bicarbonate alkalinity, and the presence of vinyl chloride plumes provides circumstantial evidence that fuel hydrocarbon co-contamination may be an important factor in the reductive dehalogenation of CVOC plumes in the historical case analysis data set. Elevated manganese concentrations at sites with vinyl chloride plumes is consistent with the presence of an anaerobic environment at these sites. Field evidence suggesting the association between fuel hydrocarbons and reductive dehalogenation has been observed anecdotally by workers at a number of sites (Wiedemeier et al., 1996). The statistical results of the CVOC historical case analysis imply that the phenomenon may be widespread.

It is important to recognize, however, that the West Coast-bias in the site representation in the data set may influence these results. For example, sites from the eastern U.S., characterized by higher precipitation and often a greater preponderance of vegetation, may be characterized by larger quantities of natural organic carbon, which would be available to facilitate reductive dehalogenation. In such instances, the influence of fuel hydrocarbon co-contamination may be less pronounced. A data set that is more uniformly representative of climatic conditions across the U.S. would be required to further illuminate this issue.

The potential association of reductive dehalogenation processes with fuel hydrocarbon co-contamination raises the issue of how long reductive dehalogenation may be sustained at many of these sites. For example, if the source of fuel hydrocarbons is depleted prior to the dissipation of the CVOC plume(s) and a CVOC source still persists, the rate of reductive dehalogenation may be significantly reduced and result in a period of plume growth. This possibility is difficult to address with the data at hand from most of the sites in the CVOC historical case analysis, particularly the lack of historical data over a sufficiently long monitoring period. Thus, while the analysis of site data presented in this study provides a snapshot in time of recent plume behavior, attempts to predict the effect that fuel hydrocarbon presence may have on CVOC plume behavior in the future must be treated as a site-specific issue.



## 5. Discussion and Recommendations for Future Work

It is clear that variability is a fundamental characteristic of CVOC sites and that conclusions stemming from the current study are general and should not be strictly applicable at any specific site. Although the emphasis in this study is on examining correlations between plume length and hydrogeologic variables, it is apparent that there is enormous variability in both plume length and maximum concentration. For example, plume lengths span two orders of magnitude while maximum concentrations span over four orders of magnitude. Though the numbers of sites in parts of the country other than the West Coast are limited, it appears that variability in plume length and reported maximum concentration occurs in all regions of the country. The addition to the data set of more sites from around the country may show that West Coast sites fully span the range for all CVOC plumes in terms of length, concentration, and site characteristics. However, this cannot be concluded with certainty until the data set is populated with sites from a broader geographic distribution. Indeed, there is no way of ascertaining whether or not the data set presents an unbiased sample of the entire population of CVOC plumes across the U.S. without completing a survey that better represents all the hydrogeographic settings in the U.S.

Continued data collection is recommended because a more comprehensive data set would shed light on some of the questions not answered completely in this present study. These questions include:

- Are there significant differences in plume behavior across different geographic and hydrogeologic regimes (e.g., as specified in Heath, 1984)?
- Is there a dependence of plume behavior on climatic factors such as mean annual rainfall, evapotranspiration rate, or vegetative cover at the site?
- What is the quantification of statistical relationships between site natural organic carbon content and (1) retardation of plume length or normalized plume length and (2) reductive dehalogenation? With regard to reductive dehalogenation in particular, a comparison of the roles of natural organic carbon and anthropogenic carbon sources (e.g., fuel hydrocarbons) would be of significant interest. The finding of the present study that reductive dehalogenation is closely related to the presence of fuel hydrocarbons may be a reflection of a bias in the data set toward the more arid (i.e., low organic carbon content) sites from the western U.S.
- Are there differences in the relationships of plume behavior to site variables, particularly the classes of plumes specifically excluded from this study, e.g., plumes that daylight. As discussed previously, the use of exclusion criteria may systematically under-represent very short and very long plumes in the data set.

In summary, this study sets a precedent for future historical case analysis studies that might include:

1. More detailed analyses of retardation phenomena contingent upon availability of soil TOC data.

2. Geostatistical analyses of plume spatial moments to include dispersion (in three dimensions) as a variable.
3. Development of a significantly expanded data set (i.e., hundreds of sites) that would allow subsets of site classes to be evaluated separately and then be compared to each other.

The ultimate goal of such follow-on studies should be to develop a comprehensive statistical model for plume behavior. This statistical model could provide:

1. Individual site investigators with a plume reference model against which a given plume may be compared and used to identify anomalous behavior.
2. Regulatory agencies with an integrated survey of plume behavior under a variety of conditions.
3. Validation for theoretical models and anecdotal studies of plume behavior within a probabilistic conceptual framework.

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# **Appendix A**

## **Analysis of Field Data**

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# **Appendix A**

## **Analysis of Field Data**

### **A-1. Physical Variables and Plume Length**

#### **A-1.1. Source Strength**

Non-aqueous phase liquids (DNAPLs), present in the subsurface as ganglia or droplets above or below the water table, often constitute a source of new dissolved-phase contaminants to the expanding plume. In practice, because of its elusive nature, any DNAPL present at a site is extremely difficult to identify or quantify (Feenstra et al., 1996). As a result, rules-of-thumb pertaining to the maximum concentrations observed at a site are often used to flag the possible occurrence of DNAPL. For example, Feenstra and Cherry (1988) proposed that measured concentrations of a given CVOC in groundwater monitoring wells at a site that exceed 10% of its solubility may be reflective of DNAPL. Newell and Ross (1991) proposed a more conservative threshold of 1% of the solubility limit.

Taking these rules-of-thumb at face value, maximum observed historical concentrations may be used to define three levels of confidence as to the possibility that DNAPL material is contributing to a dissolved plume. In cases where maximum concentration of a given CVOC exceeds 10% of its solubility, DNAPL may be assumed as likely to contribute to the plume. If the maximum concentration falls between 1% and 10% of the solubility, DNAPL may be assumed as possibly contributing to the plume. Finally, if the maximum concentration is less than 1% of the solubility, DNAPL may be assumed to not be present or else not be contributing significantly to the plume.

Using these definitions, the association of potential DNAPL sources with plumes representing the most common CVOCs in the data set (i.e., CVOCs represented by 10 or more plumes) are given in Table A-1. There appears to be some distinction between the presumed presence of DNAPLs with regard to likely original contaminants – TCE, PCE, and 1,1,1-TCA – and potential transformation daughter products – *cis*-1,2-DCE, 1,1-DCE, 1,1-DCA, and vinyl chloride. However, this observation simply be a reflection of greater use of the former group as opposed to the latter in industrial operations, hence a greater likelihood of encountering high concentrations indicative of DNAPL.

A more general analysis of the relationship between plume length and the maximum observed historical concentration would assume that the latter simply reflects the overall strength of the source term. This source strength term entails not only the presence or absence of DNAPL but also the potential for high concentrations of a CVOC (which may or may not be associated with DNAPL) to leach into the monitored portion of the aquifer. Correlation relationships between plume length and maximum historical concentrations for all CVOCs across all of the sites are shown on Figure A-1. Although a great deal of scatter is present in these relationships, statistically significant correlations are apparent. The scatter in these relationships is produced

by: (1) dependence of plume length on other variables beside source strength, and (2) variability among the sites as to how well the high concentrations immediately associated with the source are reflected in water quality measurements. The greater correlation between plume length and maximum concentration apparent with 100- and 1000-ppb plumes in comparison to 10-ppb plumes may be associated with the greater proximity of the higher concentration contours to the source area. In the case of 10-ppb-defined plumes, with the leading edge far downgradient of the source area, variability in groundwater velocity and other factors may reduce the impact of source strength variability (McNab and Dooher, 1998).

### **A-1.2. Advection**

Among the 65 sites that provided data for this study, hydraulic conductivity values were available from 46 sites at the time of analysis. In some cases, these were provided as a table of conductivity estimates derived from pumping tests or slug tests in multiple groundwater monitoring wells. In other cases, a range of values consisting of a minimum and maximum value for the site was provided. In both of these situations, given the lognormal distribution of hydraulic conductivity values characterizing most hydrogeologic settings, a representative hydraulic conductivity was estimated for the site using the geometric mean. In still other cases, some sites provided only a single interpreted mean hydraulic conductivity value for a site.

Of the sites that supplied hydraulic conductivity estimates, mean hydraulic gradient estimates were given in the hydrogeologic data from 34 sites. This permitted the calculation of a mean groundwater velocity at each of these sites using Darcy's law (assuming a universal average porosity of 0.25). The resulting probability distribution of groundwater velocities from these sites is shown on Figure A-2. This velocity distribution is reasonable in terms of groundwater velocities generally reported in shallow sedimentary materials. For example, Mackay et al. (1985) provided an estimate range of typical groundwater velocities on the order of 1 to 100 m/yr (0.009 ft/day to 0.9 ft/day).

The relationship between the maximum CVOC plume length at each site and the groundwater velocity is shown on Figure A-3. Maximum plume length at each site was used for this analysis, rather than all site plume lengths, because the longest plumes presumably reflect a better average of site conditions than small plumes which may attenuate as a result of insufficient mass. Furthermore, including all of the CVOC plume lengths at a given site in this analysis would result in a bias toward those sites with more plumes. At sites where ranges of hydraulic conductivity values were provided, the error bars denote the minimum and maximum groundwater velocities, assuming a single value for both hydraulic gradient and porosity. The scatter plot is shown with the independent variable (log groundwater velocity) on the y-axis to facilitate inspection of the error bars. A positive correlation clearly exists between the mean groundwater velocity and maximum site plume length. Some degree of mutual correlation between minimum groundwater velocity, maximum groundwater velocity, and maximum site plume length is also apparent.

Although a relationship between plume length and groundwater velocity is intuitive in a mechanistic sense, the identification of this relationship in field data is not immediately straightforward. Hydraulic conductivity and groundwater velocity are well known to vary greatly across a given site, thus defining a mean hydraulic conductivity and velocity may be problematic at first glance. Relying on only the maximum velocity at each site as an indicator of



advection, based on the assumption that the plume will travel only through the most permeable channels, may not be an acceptable substitute. This is because, without further information, the continuity of the most permeable bodies and their mutual inter-connectiveness cannot be ascertained. In contrast, the mean hydraulic conductivity and hence mean groundwater velocity may reflect the preponderance of a certain lithology at a given site (i.e., a generally coarse-grained sedimentary environment versus a fine-grained one) and thus provide a better qualitative guide to the potential for plume migration.

### **A-1.3. Additional Factors: Plume Age and Macrodispersion**

Intuitively, the overall age of a plume would be expected to exert an effect on plume length. Clearly, the longer a source of contamination is active, or the longer the elapsed time since an instantaneous release had occurred, the longer advective and dispersive transport mechanisms have had the opportunity to act on the plume. The obvious expectation is that older plumes should be longer than younger ones. Unfortunately, precise quantification of release history associated with typical CVOC groundwater contamination sites is not usually possible. However, there is likely to be some correlation between the age of a CVOC plume and the duration of industrial operations at a release site. Thus, the variability in plume age may be reflected in the distribution of site operation times observed in the project data set (Fig. A-4).

The relationship between plume length, calculated groundwater velocity, and the elapsed time of site operations for 30 TCE plumes is shown on Figure A-5. The size of the circles indicates the elapsed period of site operations, and the shade of the disk represents the range of maximum historical TCE concentration. The longest plume (A) shown on Figure A-5 exhibits a maximum historical concentration of less than 1,000 ppb, but is characterized by an elapsed site operation period of 48 years and corresponds to the second highest pore water velocity (34 ft/day). The next longest plume (B) exhibits a pore water velocity of 0.27 ft/day and a relatively large maximum concentration (56,330 ppb). An adjacent plume on the figure, Plume C, is characterized by a pore water velocity four times as large, but with a maximum concentration 1/200th as large. The shortest plume (D) corresponds to the second smallest pore water velocity and a maximum historical concentration between 1,000 and 10,000 ppb. In general, plumes from sites with the shortest elapsed operational history are among the shortest, with two noticeable exceptions, (E) and (F). In summary, some plumes are consistent with simple hydrologic reasoning, while others may be influenced by either heterogeneity within the site that is poorly represented in the averaged data or other variables. Note that five (out of seven) of the TCE plumes with maximum concentrations greater than 100,000 ppb do not appear on this figure because mean hydraulic gradient values, used in the calculation of the pore water velocity, were not available for those sites. This lack of hydrogeological data provides an example of the difficulty of analyzing the present data set in which not all site data are available at each site. Such limitations inherent in the data point to the need for caution in the application of statistical analyses to this data set.

In general, while the variability in age would be expected to exert some effect on plume length distributions, this effect is probably relatively minor in comparison with those of other variables. For example, a difference in plume age of only a factor of 2 or 3 is very small in comparison to variability in mean groundwater velocity, which varies over orders-of-magnitude

(Fig. A-2). Thus, the latter factor is likely to exert a much larger influence on plume length variability than the former.

In addition to the mean rate of advection at a site, macrodispersion resulting from a heterogeneous flow field, matrix diffusion, and other effects would also be expected to impact plume length as defined in the context of this study. However, because plume dispersion is a mathematical concept which averages the effects of a number of processes occurring on small spatial scales relative to the overall size of the plume, there are no measurable variables available from field sites with which to perform correlation analyses. Hence, plume macrodispersion was not considered in these analyses.

## **A-2. Transformation Processes and Plume Length**

### **A-2.1. Reductive Dehalogenation**

#### ***A-2.1.1. Site Categorization***

The primary mechanism responsible for the breakdown of CVOC compounds in certain groundwater biogeochemical settings is reductive dehalogenation (Bouwer et al., 1981; Vogel et al., 1987; Freedman and Gosset, 1989; Lee et al., 1995; Semprini et al., 1995; Butler and Barker, 1996; McCarty, 1996). This process, the sequential replacement of chlorine atoms with hydrogen atoms on the CVOC molecule, involves electron transfer and is microbiologically mediated. Because the reaction is a chemical reduction, reductive dehalogenation is generally observed only in anaerobic environments. Ideally, for purposes of this study, mean CVOC biotransformation rates would be quantified as continuous variables at sites where reductive dehalogenation is occurring. Statistical analyses of potential relationships between the mean biotransformation rate and plume length could then be conducted. However, given the limited spatial and temporal data available from many of the sites in the study, the systematic quantification of biotransformation rates at most of the sites was not feasible. Therefore, reductive dehalogenation was treated as a categorical variable.

Assignment of a reductive dehalogenation category to plumes at a given site was based primarily upon the presence of likely daughter products, such as *cis*-1,2-DCE or vinyl chloride derived from partial dechlorination of TCE or PCE. To evaluate reductive dehalogenation in this study, sites were categorized according to the presence or absence of these two potential daughter products. Specifically, sites with chloroethene plumes were assumed to:

1. Exhibit no reductive dehalogenation if *cis*-1,2-DCE and vinyl chloride plumes were both absent (No RD sites),
2. Exhibit some reductive dehalogenation activity if a *cis*-1,2-DCE plume was present, but a vinyl chloride plume was absent (Weak RD sites), or
3. Exhibit the highest degree of reductive dehalogenation activity if a vinyl chloride plume was present (Strong RD sites).

This classification scheme is based on the assumption that stronger reducing conditions are required to produce vinyl chloride than *cis*-1,2-DCE (Vogel et al., 1987). In all, 23 sites fell in the first category (no reductive dehalogenation), 18 in the second category (weak reductive

dehalogenation), and 20 in the third category (strong reductive dehalogenation). Three sites could not be characterized because chloroethenes were absent altogether, while an additional site could not be characterized because the detection limits for potential daughter product compounds were too high to allow the presence or absence of daughter plumes to be ascertained.

Possible geochemical indicators of reductive dehalogenation provide an independent means for testing the integrity of the categorization scheme. Concentration distributions of four key geochemical indicators (e.g., chloride ion, manganese, total xylenes, and bicarbonate alkalinity) were compared among the sites assigned to the three reductive dehalogenation categories. Ideally, elevated chloride concentrations would be expected in association with reductive dehalogenation, while elevated fuel hydrocarbon concentrations (as xylenes) and elevated bicarbonate would indicate the presence of a carbon source to fuel the reductive dehalogenation process. Manganese is reflective of the groundwater oxidative-reductive chemistry; elevated concentrations would indicate an anaerobic environment favorable for reductive dehalogenation whereas low concentrations would be indicative of an unfavorable aerobic environment. At each site where one or more of these concentrations of these geochemical indicators were provided, the 90<sup>th</sup> percentile value was noted for the indicator(s). The median values among the 90<sup>th</sup> percentile concentrations for each indicator for each reductive dehalogenation category are given in Table A-2. Taken as a whole, the geochemical indicators are consistent with expectation in terms of the potential for reductive dehalogenation. For example, in comparing the strong reductive dehalogenation sites to the other two categories, it appears that fuel hydrocarbon oxidation to bicarbonate alkalinity is a common phenomenon, producing an anaerobic environment (hence elevated manganese) resulting in dechlorination of the CVOCs (hence elevated chloride). Nevertheless, these findings must be treated with caution as the null hypothesis *p*-values suggest some uncertainty in these patterns, particularly for chloride and manganese.

#### ***A-2.1.2. Reductive Dehalogenation and Plume Length***

The most straightforward analysis of the effects of reductive dehalogenation on CVOC plume length is to compare plume length distributions of all CVOC plumes from each reductive dehalogenation site category. Cumulative plume length distributions and idealized frequency distributions (based on a lognormal distribution best-fit to the data) for the three categories are shown on Figure A-6 (both with and without the *cis*-1,2-DCE and vinyl chloride daughter products). The close overlap of the distributions among the categories suggests that the influence of reductive dehalogenation processes on plume length is rather subtle in comparison to other variables that may exert more significant influences.

Given the observed patterns in the data set, identification and quantification of reductive dehalogenation effects requires factoring out the effects of demonstrably significant variables, namely the source strength and the groundwater velocity. One means for accomplishing this is to define a *plume length index* (PLI) that adjusts plume length based on a presumed linear dependence on maximum concentration and groundwater velocity:

$$PLI = \frac{L}{C_{\max} v} \quad (\text{Eq. A-1})$$

where  $L$  refers to the observed plume length,  $C_{max}$  the maximum observed historical concentration for the particular CVOC, and  $v$  the mean site groundwater velocity. Short plume lengths relative to high  $C_{max}$  and  $v$  may reflect attenuation processes such as reductive dehalogenation.

Cumulative distributions of plume length indices and best-fit lognormal frequency distributions for CVOC plumes from each reductive dehalogenation category are shown on Figure A-7. Plume length indices from sites in the Strong RD category (i.e., vinyl chloride plume present) exhibit significantly smaller plume length indices. For example, the null hypothesis  $p$ -value given by the application of the student's  $t$ -test to logarithms of the data indicate  $p = 0.98$  for the raw plume lengths alone (i.e., plume length distributions are similar) for the No RD and Strong RD groups, whereas  $p = 0.002$  for these groups using the PLI (i.e., plume length index distributions are distinct). These patterns exist regardless of whether or not the daughter product species (*cis*-1,2-DCE and vinyl chloride) are excluded from the analyses. Thus, the plume length index concept demonstrates differences in plume behavior between sites featuring vinyl chloride plumes and those that do not, whereas such differences are not readily apparent upon first inspection of plume lengths alone.

There are at least two explanations as to why the effect of reductive dehalogenation on plume length is not immediately apparent in the raw plume length data but is identifiable in the plume length indices. One is simply that noisy data preclude the ready identification of subtle trends, and that the indexing scheme removes enough of the noise element so that such trends may become apparent. This possibility is explored in this study using a probabilistic plume modeling approach (see discussion below). The second possibility is that the overlap of raw plume length distributions reflects biases in the data collection and reporting process. For example, plumes undergoing strong reductive dehalogenation at sites with low groundwater velocities and small source terms would tend to be relatively short, hence not well characterized, and thus may have been excluded from the data collection effort. Conversely, non-transforming plumes emanating from high concentration source areas at high groundwater velocity sites would tend to be quite large and hence subject to pump-and-treat remediation efforts early in the site investigation history (and therefore excluded from the study). The net result is that selectively "long" plumes undergoing reductive dehalogenation may be grouped with selectively "short" plumes from non-reductive dehalogenation sites in the data set, systematically obscuring the effects of reductive dehalogenation on plume length. Nevertheless, the range of plume lengths encountered is of the foremost interest to stakeholders, so this possible bias does not necessarily detract from the validity of the study.

The plume length index is a new concept that has not been previously suggested in the literature. Hence, for validation, the results must be buttressed by independent multivariate statistical methods. To address this need, an examination of the relationships between plume length, maximum historical concentration, groundwater velocity, and reductive dehalogenation category was conducted using analysis of covariance (ANCOVA) along with a general linear model (GLM). The findings of these analyses are entirely consistent with those suggested by the plume length indices; plume length is affected by reductive dehalogenation (Strong RD data set) once the effects of source strength and groundwater velocity are accounted for. This appears to be true regardless of whether or not *cis*-1,2-DCE and vinyl chloride plumes are considered in the analyses. The ANCOVA and GLM analyses are presented in Appendix C.

### ***A-2.1.3. Daughter Product Plumes***

Given that reductive dehalogenation occurs, in principle, in a sequential manner, daughter product plumes will develop in association with the parent plume. If the daughter product species are not readily transformed into subsequent degradation products, these daughter product CVOCs could eventually accumulate downgradient of the parent product plume, despite the attenuation of the original contaminant compound. Given the metrics used in this study, this would complicate the task of defining the plume length associated with a given CVOC release. In the case of vinyl chloride, a daughter product of reductive dehalogenation of PCE or TCE, this extension beyond the parent plume would pose an additional problem because of the relatively high apparent toxicity of vinyl chloride in comparison to either PCE or TCE. However, if daughter product CVOCs such as vinyl chloride were readily attenuated, the daughter plumes would be largely encompassed within the original parent product plume, and risk-management characterization and constraints on the parent plume would also address the daughter products as well.

Statistical evidence collected in this study suggests that large daughter product plumes in comparison to the parent product plumes are not the norm but rather the exception. There are three lines of evidence to support this finding:

1. Among all of the CVOCs represented by more than six 10-ppb-defined plumes in the data set, analysis of variance (ANOVA) suggests that there is no statistically significant difference among logarithms of plume lengths by CVOC.
2. At sites with co-existing parent and daughter product CVOCs (among TCE, *cis*-1,2-DCE, and vinyl chloride), the parent CVOC plume length is indicated as being longer than corresponding daughter plume length(s) in 73% of the cases (37 out of 51 cases).
3. The locations at which maximum historical concentrations of parent and daughter product CVOCs are measured are typically separated from one another by distances on the order of 10% to 25% of the longest plume length at the given site. In other words, the source areas of daughter plumes are not greatly offset from parent plumes in most instances.

To gain further insight into the spatial relationships between parent and daughter product CVOC plumes, TCE and vinyl chloride plumes (as defined by the 10-ppb contour) were compared at the 17 sites where both coexisted. The mean direction that each CVOC plume at was headed at each site was estimated by quantifying the angle formed by the sentry well (the well farthest from the presumed source area with a concentration greater than 10 ppb), the well exhibiting the maximum historical concentration, and due east. Presumably, both parent and daughter plumes should be sub-parallel to one another; departures from this would indicate poorly characterized, ill-defined plumes or spatially variable biogeochemical processes yielding daughter product plumes of irregular shape. The resulting distribution in the differences between the directions of TCE and vinyl chloride plumes among the 17 sites are shown on Figure A-8. The distribution is clearly bimodal, with one group exhibiting sub-parallel plumes (generally less than 20° apart), with the other group featuring approximately anti-parallel plumes (near 180° apart).

Among the 11 sites in the sub-parallel group, the respective measurement locations of the maximum historical concentrations of TCE and vinyl chloride differ from one another by a

distance equivalent to about 15% (median value) of the maximum plume length (TCE or vinyl chloride). In other words, within this group of sites, the areas of maximum concentration of the parent and daughter plumes are roughly co-located. At the same time, TCE plume lengths are, as a group, longer than the respective vinyl chloride plumes in this set of sites, with the median ratio of TCE-to-vinyl chloride plume length approximately 1.6. Only 3 of the 11 sites featured a vinyl chloride plume length that appeared longer than that of the corresponding TCE plume (by 7%, 12%, and 23%, respectively).

The second set of sites consisted of six examples where the parent and daughter plumes appeared to the plume length algorithm to be oriented in approximately opposite directions. This was generally the result of the maximum historical concentration of vinyl chloride being observed a significant distance downgradient of the maximum concentration location of the TCE plume. Indeed, the median separation distance between the TCE and vinyl chloride maximum concentration locations was approximately 55% of the maximum plume length at each site. A number of possible explanations exist for this phenomenon, including: (1) high analytical detection limits for vinyl chloride in the presence of high concentrations of TCE, (2) chance artifacts of the monitoring well network spatial configuration and sampling history, (3) a detached daughter product plume reflective of very slow rates of reductive dehalogenation, or (4) spatial heterogeneity in the biogeochemical environment. Regardless of the cause(s), it is not appropriate to compare plume lengths directly in these cases because the parent and daughter plumes may not overlap. Instead, a combined TCE-vinyl chloride plume definition, derived by adding the concentrations of the two CVOCs in each groundwater sample, is a more direct reflection of the impact of CVOCs to groundwater at these sites. Application of the plume algorithm to the combined data sets from these six sites suggests that the TCE plumes, and not the vinyl chloride daughter product plumes, are the principal factors in determining the combined CVOC plume length. Combined TCE-vinyl chloride plume lengths clearly exceed those of the individual TCE plumes at only two of the six sites (by 10% and 38%, respectively).

#### ***A-2.1.4. Time Series Analysis***

Relative rates of plume growth were assessed for 141 of the 247 10-ppb-defined plumes using rank correlation (i.e., linear regression of the ranks of the plume length as the dependent variable and rank of the monitoring year as the independent variable). The qualification of plume length trends as increasing or decreasing, with student *t*-test *p*-values as a means of quantifying significance, are shown in Tables A-3(a) and (b) for plumes from the Strong RD group and those that are not, respectively. Regardless of the confidence level, the two populations of plumes do appear to differ from one another according to this analysis in that the plumes from the Strong RD group exhibit a diminished tendency toward increases in plume length than those plumes from the No RD and Weak RD groups. Previous historical case analyses of fuel hydrocarbon plumes (Rice et al., 1995, Mace et al., 1997) indicated that only a small minority of hydrocarbon plumes (on the order of 10%) were experiencing discernable plume growth, presumably as a result of the limiting effects of biotransformation processes. Thus, the differences in apparent CVOC plume growth rates provides an independent line of evidence to support the conclusion that reductive dehalogenation influences plume length behavior at sites where vinyl chloride plumes are present.

### **A-2.2. Abiotic Transformation of 1,1,1-TCA**

1,1,1-TCA is unique among the commonly encountered CVOC contaminants found in groundwater in its abiotic transformation, yielding acetic acid and 1,1-DCE as daughter products through separate pathways (Vogel and McCarty, 1987a, b; Haag and Mill, 1988; Jeffers et al., 1989; McCarty, 1996). These reactions do not rely on microbial mediation and are independent of the local groundwater geochemistry in terms of the biogeochemical redox regime. The associated pseudo-first-order half-life of 1,1,1-TCA is on the order of one to two years, depending primarily on temperature. As such, 1,1,1-TCA should serve as a marker compound for the effects of transformation processes on plume length. Cumulative probability distributions (along with best-fit lognormal frequency distributions) for 1,1,1-TCA plume lengths, compared with those of all other CVOCs, are shown on Figure A-9 (top). The median values of both groups of plume length are very similar, indicating that transformation of 1,1,1-TCA is not exerting a major effect on plume length compared to other factors (although the 1,1,1-TCA plume lengths do exhibit a tighter clustering about the mean than the other CVOCs). When plume lengths are transformed into plume length indices via Eq A-1, the plume length indices of 1,1,1-TCA appear shorter than those of the other CVOCs (Fig. A-9, bottom). The *p*-value associated with the null hypothesis for the two plume index populations (i.e., the probability that the two means are the same) is 0.14 by the student's *t*-test applied to the logarithms, suggesting a good possibility that the apparent difference is significant. However the population size of the 1,1,1-TCA plume length indices is rather small so this conclusion must be considered tentative. Nevertheless, the results are similar to those obtained from analyses of the reductive dehalogenation site categories, so similar explanations may apply to the 1,1,1-TCA data as well.

### **A-3. Partitioning Phenomena**

Partitioning relationships pertain to the distribution of CVOC mass between the aqueous, DNAPL, and gaseous phases and present another class of variables that may influence CVOC plume behavior. The effects of these partitioning relationships on CVOC plume behavior can be assessed through statistical analyses of the relationships between plume variables and partitioning coefficients. Specifically, partitioning relationships include the solubility of the CVOC in water, the vapor pressure of the CVOC DNAPL in contact with the gas phase, the distribution of mass between the aqueous and gaseous phases (Henry's Law partitioning), and adsorption of the CVOC from the aqueous phase onto the solid matrix. In this case, the properties of the individual CVOCs (i.e., solubility, vapor pressure, Henry's constant, organic carbon partitioning coefficient) are the independent variables rather than the site hydrogeologic variables. Representative values of these partitioning coefficients for the CVOCs evaluated in this study are given in Table A-4.

#### **A-3.1. Organic Carbon Partitioning**

Consider the two hypothetical release scenarios illustrated on Figure A-10. In Scenario 1, little or no organic carbon is present in the sediments at the site, so two CVOCs with very different organic carbon partitioning coefficients,  $K_{oc}$ , would tend to exhibit similar concentration distributions following release, assuming that all other factors (release volume, solubility) are equivalent. In Scenario 2, however, CVOC A would be expected to adsorb strongly onto the organic-rich material, so that the measurable aqueous-phase concentrations of CVOC A would

be significantly lower than those of CVOC B. Given this simple model and assuming a wide range of organic carbon content values across a number of sites, the more hydrophobic CVOCs (those with relatively high  $K_{oc}$  values) would be expected to show more variability in concentration than those with lower  $K_{oc}$  values.

Statistical analyses of inter-site maximum concentration variability among the CVOCs is consistent with this hypothesis. The maximum historical concentrations of individual CVOCs across multiple sites appear lognormally distributed. Given this, a coefficient of variability was defined by the standard deviation of the logarithm of maximum concentration, divided by the geometric mean of the maximum concentrations for each CVOC where at least six or more plumes exist in the data set. The relationship between the median literature-derived log  $K_{oc}$  and the observed coefficient of variability in maximum concentration is shown on Figure A-11. A significant positive correlation exists between the coefficient of variability of maximum concentration and log  $K_{oc}$ , for twelve CVOCs. If representative fractional organic carbon content ( $f_{oc}$ ) data were available from a sufficient number of sites, this possible relationship could be further assessed.

Beyond this correlation, relationships between  $K_{oc}$  and other plume variables could not be readily identified. For example, the relationship between the geometric mean plume length index and log  $K_{oc}$  is weak or absent; with correlation coefficients ( $r$ ) ranging from  $-0.22$  to  $-0.49$ , depending on the minimum number of plumes used to define geometric mean plume length index per CVOC. Additional analyses involving estimates of plume growth rates may identify relationships between the change in plume length as a function of time and the  $K_{oc}$ .

### A-3.2. Henry's Law Partitioning

Ideally, partitioning of CVOCs between the gas phase and the aqueous phase might be expected to exert effects on concentration variability similar to those suggested by the  $K_{oc}$  analyses. Consider, for example, the two hypothetical release scenarios shown on Figure A-12. In Scenario 1 (plumes in a confined aquifer) little opportunity exists for the exchange of mass from the dissolved phase into the gaseous phase in the vadose zone. Under such conditions, concentration distributions of both CVOC A and B would be expected to be similar if other variables such as release volume and  $K_{oc}$  were equivalent. In the case of plumes in an unconfined aquifer (Scenario 2), more of an opportunity would exist for the more volatile CVOC A to escape into the dissolved phase, reducing the observed aqueous concentrations in comparison to those of CVOC B. An alternative possibility would be that differences in precipitation between sites would influence the opportunity for exchange of mass across the capillary fringe. In any event, a variety of hydrogeologic or hydrologic conditions may exist across a number of sites to enhance or suppress the exchange of CVOCs between the gaseous and aqueous phases. As a result, compounds characterized by higher Henry's constants might exhibit greater variability in maximum concentration between sites than those with a low Henry's constant. The relationship between the median literature-derived log  $K_h$  and the observed coefficient of variability of maximum concentration, as defined previously, is shown on Figure A-13. A positive correlation appears to exist between the coefficient of variability and log  $K_h$ , ( $r = 0.54$ ) for the twelve CVOCs represented by six or more plumes.

Both this analysis and the previous assessment of log  $K_{oc}$  suggest that a portion the inter-site variability in maximum concentration for a given CVOC is related to both the Henry's constant



and the organic carbon partitioning coefficient. This suggests that a multivariate model may explain more of this variability than either coefficient alone. A three-dimensional scatter plot depicting such a model is shown on Figure A-14. The multivariate correlation coefficient associated with a best-fit plane to these data is approximately  $r = 0.83$ .

A weak inverse relationship is also suggested between the mean of the log plume length indices and  $\log K_h$ , ( $r = -0.48$ ) (Fig. A-15). Plume length indices can only be defined for a subset of the total plume population, as mean groundwater velocities were not available from all the sites. Thus, the eleven CVOCs included in this analysis were each represented by a minimum of three plume length indices. This relationship could conceivably reflect small losses of CVOC mass into the vadose zone from thin plumes near the water table in unconfined aquifers. After correcting for the effects of source strength and groundwater velocity, it is possible that such small mass losses may exert an effect on plume length that is detectable statistically. However, this observation is empirical at this point; it must be followed by further analyses to confirm whether or not it is a real effect.

On this last point, it is important to recognize that all of these observations regarding partitioning relationships represent statistical trends in the data that are consistent with plausible physical explanations. This does not necessarily constitute a definite proof that the explanations are indeed correct. For example, both of the Henry's Law relationships could also be explained by systematic preferential losses of the more volatile CVOCs during sample collection and handling at sites and analytical laboratories involved. Hence, these results should be regarded as tentative in nature and should be subject to further testing as additional data become available.

### **A-3.3. Solubility and Vapor Pressure**

Relationships between plume behavior and  $K_{oc}$  or  $K_h$  involve CVOCs that are dissolved in the aqueous phase. In contrast, CVOC solubility and vapor pressure partitioning relationships pertain directly to the presence of DNAPL, either in contact with the aqueous phase or the gaseous phase. Because data collection and analyses efforts associated with the present study have focused exclusively on the aqueous phase, the effects of DNAPL solubility and vapor pressure could only be assessed indirectly, i.e., as effects on CVOC mass in the aqueous phase.

No apparent relationships were identified between plume variables (geometric mean maximum concentration, coefficient of variability of maximum concentration, geometric mean plume length) and either solubility or vapor pressure based on median values noted in the literature for common CVOCs. Furthermore, the exclusion of likely daughter product CVOCs (i.e., *cis*-1,2-DCE and vinyl chloride), which would not be present as DNAPL, from the analysis did not exert any notable effect.

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**Table A-1. Fraction of plumes possibly associated with DNAPL for CVOCs represented by more than 10 plumes.**

CVOC	Total no. of 10-ppb-defined plumes	Fraction of plumes with conc.> 1% solubility	Fraction of plumes with conc.> 10% solubility
TCE	55	36% (20 plumes)	11% (6 plumes)
PCE	32	38% (12 plumes)	13% (4 plumes)
1,1-DCE	29	10% (3 plumes)	0%
<i>Cis</i> -1,2-DCE	29	7% (2 plumes)	3% (1 plume)
1,1,1-TCA	23	26% (6 plumes)	4% (1 plume)
Vinyl chloride	20	0%	0%
1,1-DCA	18	0%	0%

**Table A-2. Site median concentrations of geochemical indicator compounds from sites representing different reductive dehalogenation groups.**

Geochemical indicator species	90 <sup>th</sup> quantiles			Student t-test p-values; No RD vs. Strong RD groups
	No RD	Weak RD	Strong RD	
Cl <sup>-</sup> (mg/L)	120	162	310	0.30
Mn <sup>2+</sup> (μg/L)	130	430	1340	0.34
Total xylenes (μg/L)	6.3	8.9	74.1	0.20
Bicarbonate alkalinity (mg/L)	260	356	552	0.009

**Table A-3(a). Temporal trends in plume length for CVOC plumes from the Strong RD group characterized by monitoring data from three or more years.**

<i>p</i> -value	Decreasing length	Increasing length	No significant trend
0.01	9% (4 plumes)	4% (2 plumes)	87% (41 plumes)
0.05	11% (5 plumes)	13% (6 plumes)	77% (36 plumes)
0.1	13% (6 plumes)	15% (7 plumes)	72% (34 plumes)
0.2	21% (10 plumes)	19% (9 plumes)	60% (28 plumes)
0.3	21% (10 plumes)	26% (12 plumes)	53% (25 plumes)
0.5	23% (11 plumes)	28% (13 plumes)	49% (23 plumes)

**Table A-3(b). Temporal trends in plume length for CVOC plumes from the No RD and Weak RD groups characterized by monitoring data from three or more years.**

<i>p</i> -value	Decreasing length	Increasing length	No significant trend
0.01	9% (8 plumes)	14% (13 plumes)	78% (73 plumes)
0.05	10% (9 plumes)	21% (20 plumes)	69% (65 plumes)
0.1	12% (11 plumes)	27% (25 plumes)	62% (58 plumes)
0.2	14% (13 plumes)	34% (32 plumes)	52% (49 plumes)
0.3	17% (16 plumes)	38% (36 plumes)	45% (42 plumes)
0.5	19% (18 plumes)	44% (41 plumes)	37% (35 plumes)

Table A-4. Literature values of partitioning coefficients for CVOCs in data set.

CVOC	$K_{oc}$ (ml/g)	$K_h$ (atm m <sup>3</sup> /mol)	Solubility (mg/L)	Vapor pressure (mm Hg)
1,1-DCA	30.2 (Schwille, 1988)	4.3 x 10 <sup>-3</sup> (Mercer et al., 1990) 5.5 x 10 <sup>-3</sup> (Warner et al., 1987) 5.7 x 10 <sup>-3</sup> (Hine and Mookerjee, 1975)	5500 (Verschueren, 1983)	180 (Verschueren, 1983) 182 (Mercer et al., 1990)
1,1-DCE	64.6 (Schwille, 1988)	1.5 x 10 <sup>-2</sup> (Warner et al., 1987) 2.1 x 10 <sup>-2</sup> (Schwille, 1988) 3.0 x 10 <sup>-2</sup> (CRC Handbook, 1992) 3.4 x 10 <sup>-2</sup> (Mercer et al., 1990)	2250 (Mercer et al., 1990)	591 (Verschueren, 1983) 600 (Mercer et al., 1990)
1,1,1-TCA	104 (Chiou et al., 1979) 151 (Schwille, 1988)	1.3 x 10 <sup>-2</sup> (Schwille, 1988) 1.3 x 10 <sup>-2</sup> (Hunter-Smith et al., 1984) 1.4 x 10 <sup>-2</sup> (Mercer et al., 1990) 1.5 x 10 <sup>-2</sup> (Roberts and Dandliker, 1983) 1.6 x 10 <sup>-2</sup> (Hine and Mookerjee, 1975) 1.7 x 10 <sup>-2</sup> (Lincoff and Gossett, 1984) 1.8 x 10 <sup>-2</sup> (Lyman et al., 1982)	720 (Mackay and Shiu, 1981) 1250 (Broholm and Feenstra, 1995) 1495 (Horvath, 1982) 1500 (Mercer et al., 1990) 4400 (Verschueren, 1983)	100 (Verschueren, 1983) 123 (Mercer et al., 1990)
1,1,2-TCA	56.2 (Schwille, 1988)	1.2 x 10 <sup>-3</sup> (Mercer et al., 1990) 7.4 x 10 <sup>-4</sup> (Pankow and Rosen, 1988) 9.1 x 10 <sup>-4</sup> (Hine and Mookerjee, 1975)	4500 (Verschueren, 1983)	19 (Verschueren, 1983) 30 (Mercer et al., 1990)
1,2-DCA	14.1 (Schwille, 1988) 19 (Chiou et al., 1979)	9.1 x 10 <sup>-4</sup> (Schwille, 1988) 9.8 x 10 <sup>-4</sup> (Mercer et al., 1990) 1.1 x 10 <sup>-3</sup> (Warner et al., 1987)	8520 (Mercer et al., 1990) 8690 (Pankow et al., 1996)	61 (Mercer et al., 1990) 64 (Verschueren, 1983)
CA	17 (Mercer et al., 1990) 26.9 (Chiou et al., 1979)	8.5 x 10 <sup>-3</sup> (Hine and Mookerjee, 1975) 9.3 x 10 <sup>-2</sup> (Pankow and Rosen, 1988) 1.1 x 10 <sup>-2</sup> (Gossett, 1987) 1.5 x 10 <sup>-2</sup> (U.S. EPA, 1980)	5740 (Mercer et al., 1990)	1000 (Mercer et al., 1990)



Table A-4. (Continued)

CVOC	$K_{oc}$ (ml/g)	$K_h$ (atm m <sup>3</sup> /mol)	Solubility (mg/L)	Vapor pressure (mm Hg)
CF	43.7 (Schwille, 1988)	$2.9 \times 10^{-3}$ (Mercer et al., 1990)	7920 (Horvath, 1982)	151 (Mercer et al., 1990)
	47 (Mercer et al., 1990)	$2.9 \times 10^{-3}$ (Jury et al., 1984)	7925 (Mackay and Shiu, 1981)	160 (Verschueren, 1983)
		$3.2 \times 10^{-3}$ (Valsaraj, 1988)	8000 (Verschueren, 1983)	
		$3.2 \times 10^{-3}$ (Dilling, 1977)	8200 (Mercer et al., 1990)	
		$3.4 \times 10^{-3}$ (Warner et al., 1987)	8700 (Broholm and Feenstra, 1995)	
		$3.9 \times 10^{-3}$ (Nicholson et al., 1984)		
		$4.3 \times 10^{-3}$ (Lincoff and Gossett, 1984)		
		$5.3 \times 10^{-3}$ (Roberts and Dandliker, 1983)		
CM	25.1 (Chiou et al., 1979)	$6.6 \times 10^{-3}$ (Pankow and Rosen, 1988)	4000 (Verschueren, 1983)	3800 (Verschueren, 1983)
	35 (Mercer et al., 1990)	$8.8 \times 10^{-3}$ (Gossett, 1987)	6500 (Mercer et al., 1990)	4310 (Mercer et al., 1990)
		$1.0 \times 10^{-2}$ (Hine and Mookerjee, 1975)	7400 (Lyman et al., 1982)	
		$4.4 \times 10^{-2}$ (Mercer et al., 1990)		
CTET	224 (Abdul et al., 1987)	$2.3 \times 10^{-2}$ (Jury et al., 1984)	757 (Mercer et al., 1990)	90 (Verschueren, 1983)
	417 (Chin et al., 1988)	$2.4 \times 10^{-2}$ (Mercer et al., 1990)	780 (Broholm and Feenstra, 1995)	
	437 (Schwille, 1988)	$2.4 \times 10^{-2}$ (Robert and Dandliker, 1983)	785 (Pankow et al., 1996)	
		$2.4 \times 10^{-2}$ (Hunter-Smith et al., 1984)	793 (Horvath, 1982)	
		$3.0 \times 10^{-2}$ (Warner et al., 1987)	1000 (Mackay and Shiu, 1981)	
PCE	210 (Chiou et al., 1979)	$2.9 \times 10^{-3}$ (Warner et al., 1987)	150 (Verschueren, 1983)	14 (Verschueren, 1983)
	263 (Abdul et al., 1987)	$1.3 \times 10^{-2}$ (Schwille, 1988)	200 (Pankow et al., 1996)	17.8 (Mercer et al., 1990)
	363 (Schwille, 1988)	$1.5 \times 10^{-2}$ (Pankow and Rosen, 1988)		20 (Standen, 1964)
		$1.8 \times 10^{-2}$ (Lincoff and Gossett, 1984)		
		$2.6 \times 10^{-2}$ (Mercer et al., 1990)		

Table A-4. (Continued)

CVOC	$K_{oc}$ (ml/g)	$K_h$ (atm m <sup>3</sup> /mol)	Solubility (mg/L)	Vapor pressure (mm Hg)
TCE	64.6 (Abdul et al., 1987)	9.1 x 10 <sup>-3</sup> (Pankow and Rosen, 1988)	1050 (Mackay and Shiu, 1981)	58 (Mercer et al., 1990)
	106 (Garbarini and Lion, 1986)	9.1 x 10 <sup>-3</sup> (Mercer et al., 1990)	1100 (Horvath, 1982)	60 (Verschueren, 1983)
	126 (Schwille, 1988)	9.9 x 10 <sup>-3</sup> (Roberts and Dandliker, 1983)	1100 (Verschueren, 1983)	
		1.0 x 10 <sup>-2</sup> (Lincoff and Gossett, 1984)	1400 (Broholm and Feenstra, 1995)	
		1.2 x 10 <sup>-2</sup> (U.S. EPA, 1980)		
VC	2.5 (Karickhoff et al., 1979)	1.1 x 10 <sup>-2</sup> (CRC Handbook, 1992)	1100 (Verschueren, 1983)	2660 (Mercer et al., 1990)
	57 (Mercer et al., 1990)	2.2 x 10 <sup>-2</sup> (Pankow and Rosen, 1988)	2670 (Mercer et al., 1990)	
		5.6 x 10 <sup>-2</sup> (Hine and Mookerjee, 1975)		
		8.2 x 10 <sup>-2</sup> (Mercer et al., 1990)		
		1.2 (Dilling, 1977)		
		2.4 (Jury et al., 1984)		
		2.8 (Gossett, 1987)		
<i>Cis</i> -1,2-DCE	22.9 (Kenaga, 1980)	1.3 x 10 <sup>-3</sup> (Pankow and Rosen, 1988)	800 (Verschueren, 1983)	200 (Verschueren, 1983)
	47.9 (Schwille, 1988)	3.6 x 10 <sup>-3</sup> (U.S. EPA, 1980)	3500 (Mercer et al., 1990)	208 (Mercer et al., 1990)
		7.6 x 10 <sup>-3</sup> (Mercer et al., 1990)		
<i>Trans</i> -1,2-DCE	58.9 (Schwille, 1988)	5.3 x 10 <sup>-3</sup> (U.S. EPA, 1980)	600 (Verschueren, 1983)	324 (Mercer et al., 1990)
		6.6 x 10 <sup>-3</sup> (Mercer et al., 1990)	6300 (Mercer et al., 1990)	
		7.2 x 10 <sup>-3</sup> (Pankow and Rosen, 1988)		
MeCl	8.7 (Schwille, 1988)	2.0 x 10 <sup>-3</sup> (Mercer et al., 1990)	20,000 (Verschueren, 1983)	349 (Verschueren, 1983)
		2.9 x 10 <sup>-3</sup> (Lincoff and Gossett, 1984)		362 (Mercer et al., 1990)
1,1,2,2-TCA	46 (Chiou et al., 1979)	3.8 x 10 <sup>-4</sup> (Mercer et al., 1990)	2900 (Verschueren, 1983)	5 (Verschueren, 1983)
	117 (Schwille, 1988)	3.8 x 10 <sup>-4</sup> (Pankow and Rosen, 1988)		
		4.6 x 10 <sup>-4</sup> (Hine and Mookerjee, 1975)		

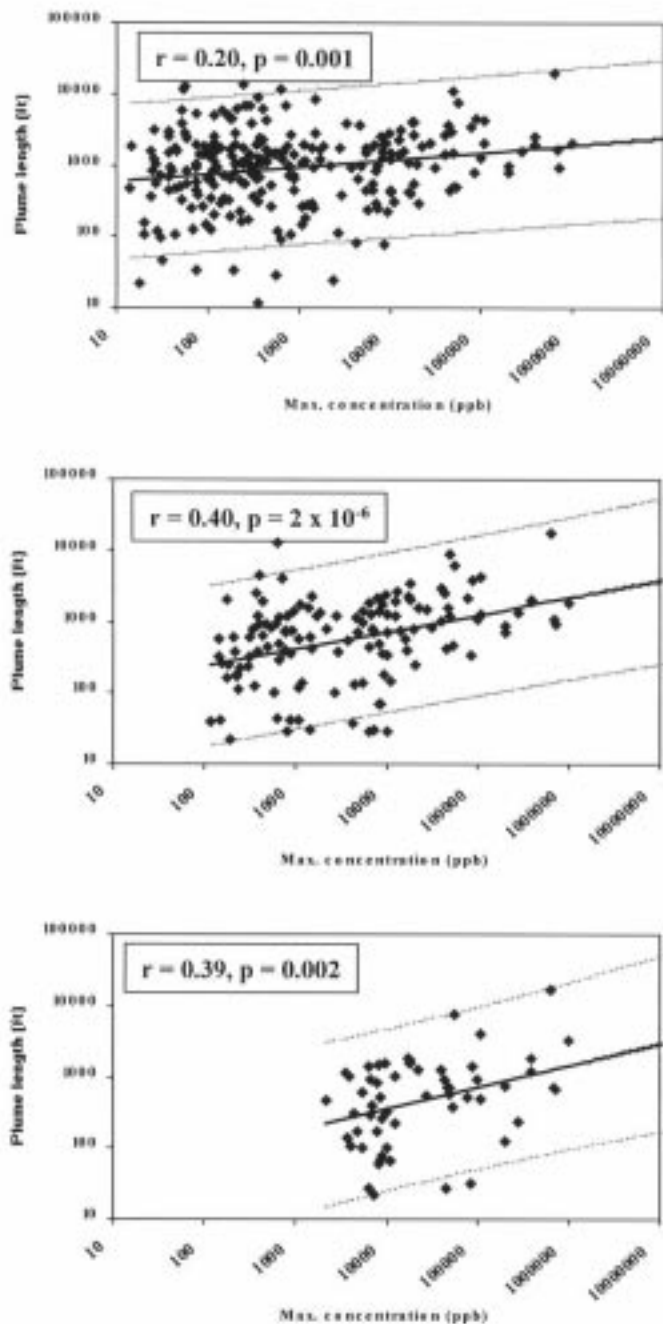


Figure A-1. Correlation between log plume length and log maximum historical concentration (per CVOC) for 10-ppb-defined plumes (top), 100-ppb-defined plumes (middle), and 1000-ppb-defined plumes (bottom). Null hypothesis probabilities are indicated by  $p$ -values. Dashed lines denote the 95% prediction confidence band.

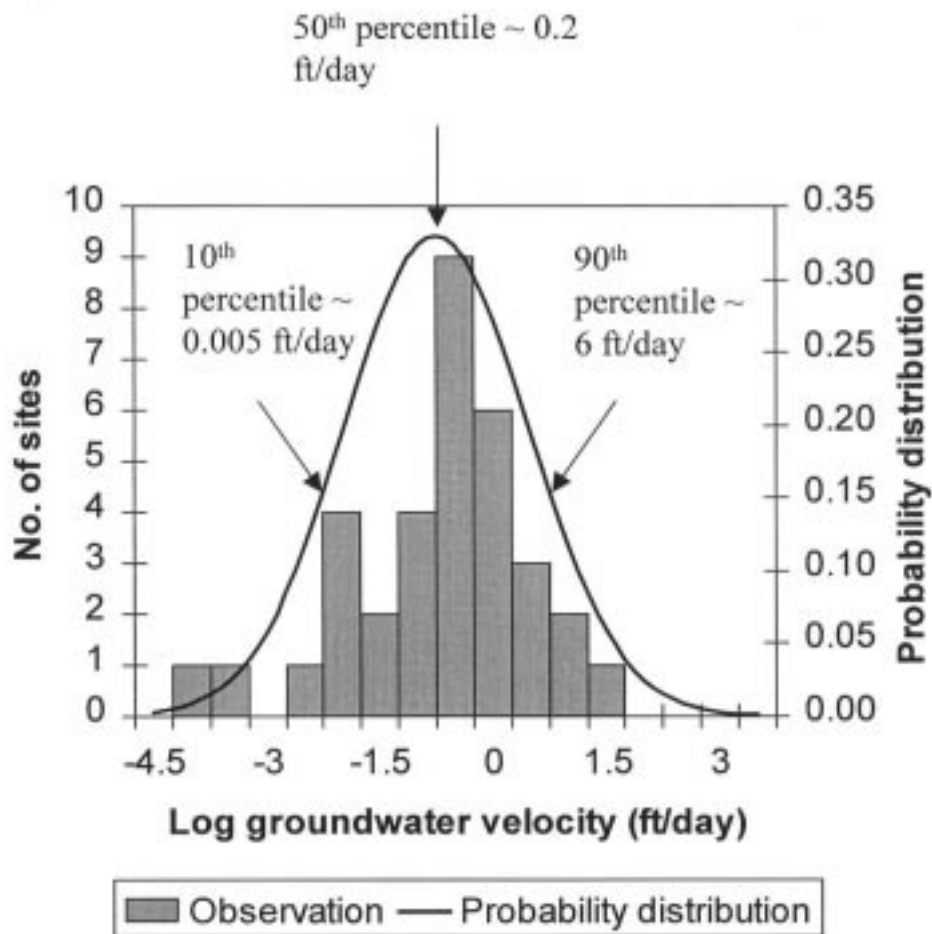


Figure A-2. Histogram and best-fit lognormal probability distribution of groundwater velocities from the 34 sites that provided hydraulic conductivity and gradient estimates.

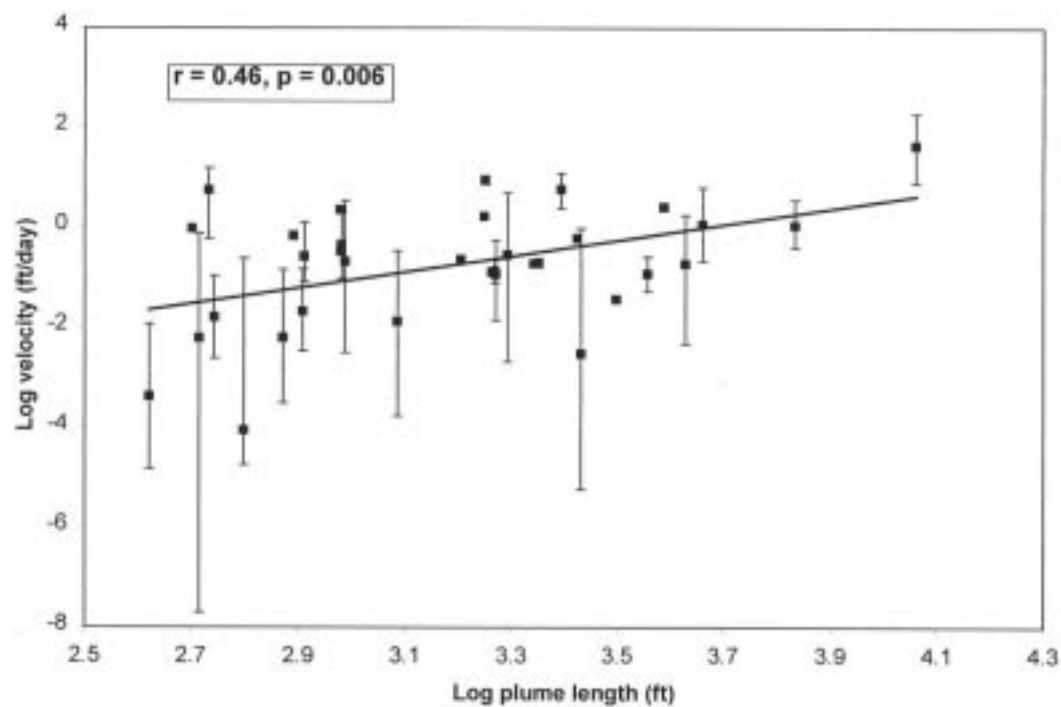


Figure A-3. Relationship between log maximum plume length per site and mean log site groundwater velocity (square symbols), with uncertainty bars showing ranges of velocity calculated from site-specific minimum and maximum hydraulic conductivity values. The independent variable, log groundwater velocity, is plotted on the y-axis to facilitate inspection of the uncertainty bars.

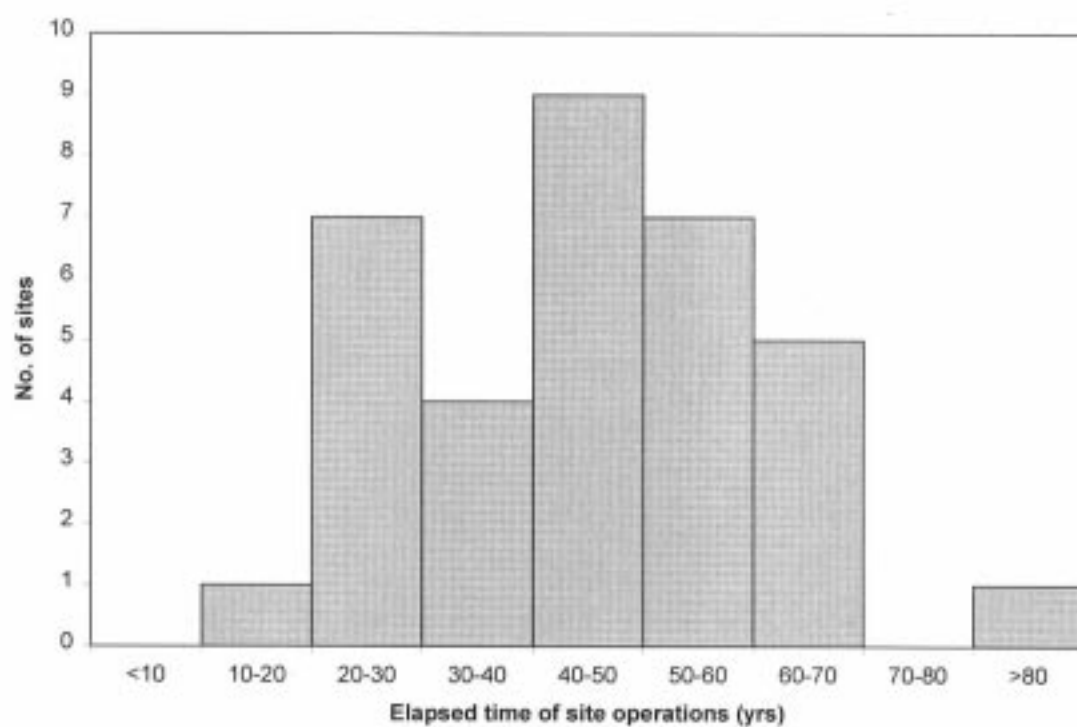


Figure A-4. Distribution of plume ages from sites in the data set reporting operational history, inferred from elapsed time of site operations.

Color of symbol represents range of maximum historical TCE concentration.  
 Black: > 100,000 ppb. Dark gray: between 10,000 and 100,000 ppb.  
 Light gray: between 1,000 and 10,000 ppb. White: < 1,000 ppb.

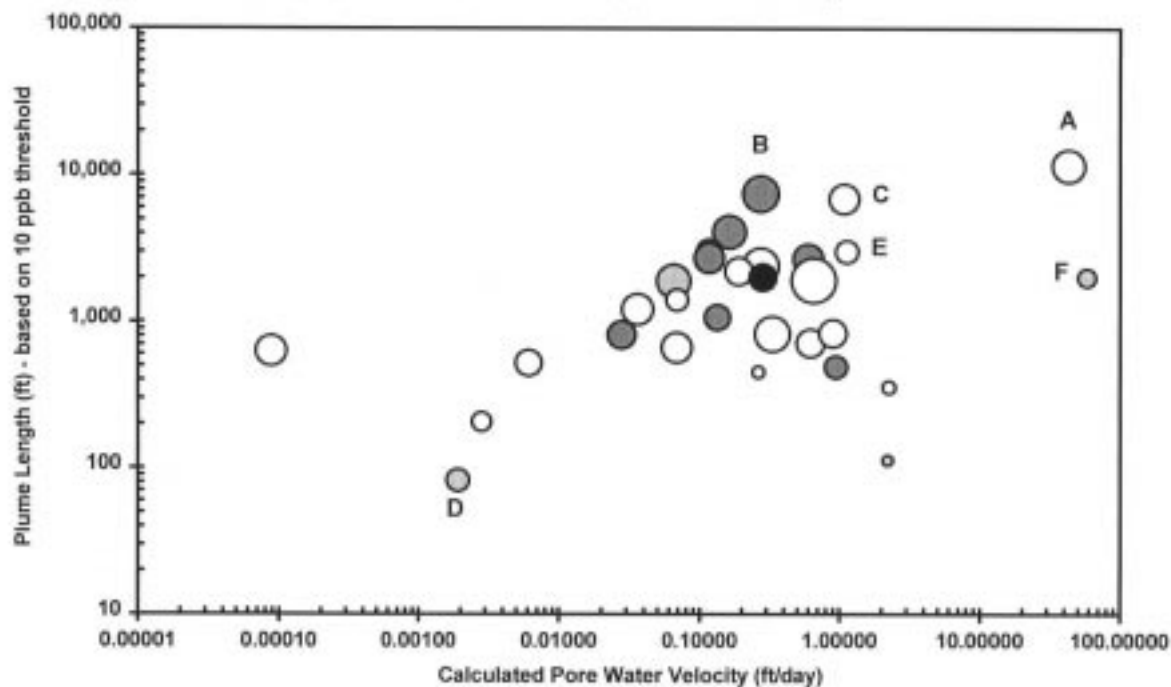


Figure A-5. Distribution of TCE plumes with respect to calculated plume length and calculated pore water velocity. The circle size represents the estimated age of the plume, and the shading of the disk represents the range of maximum concentration as indicated. See text for explanation of labeled points.

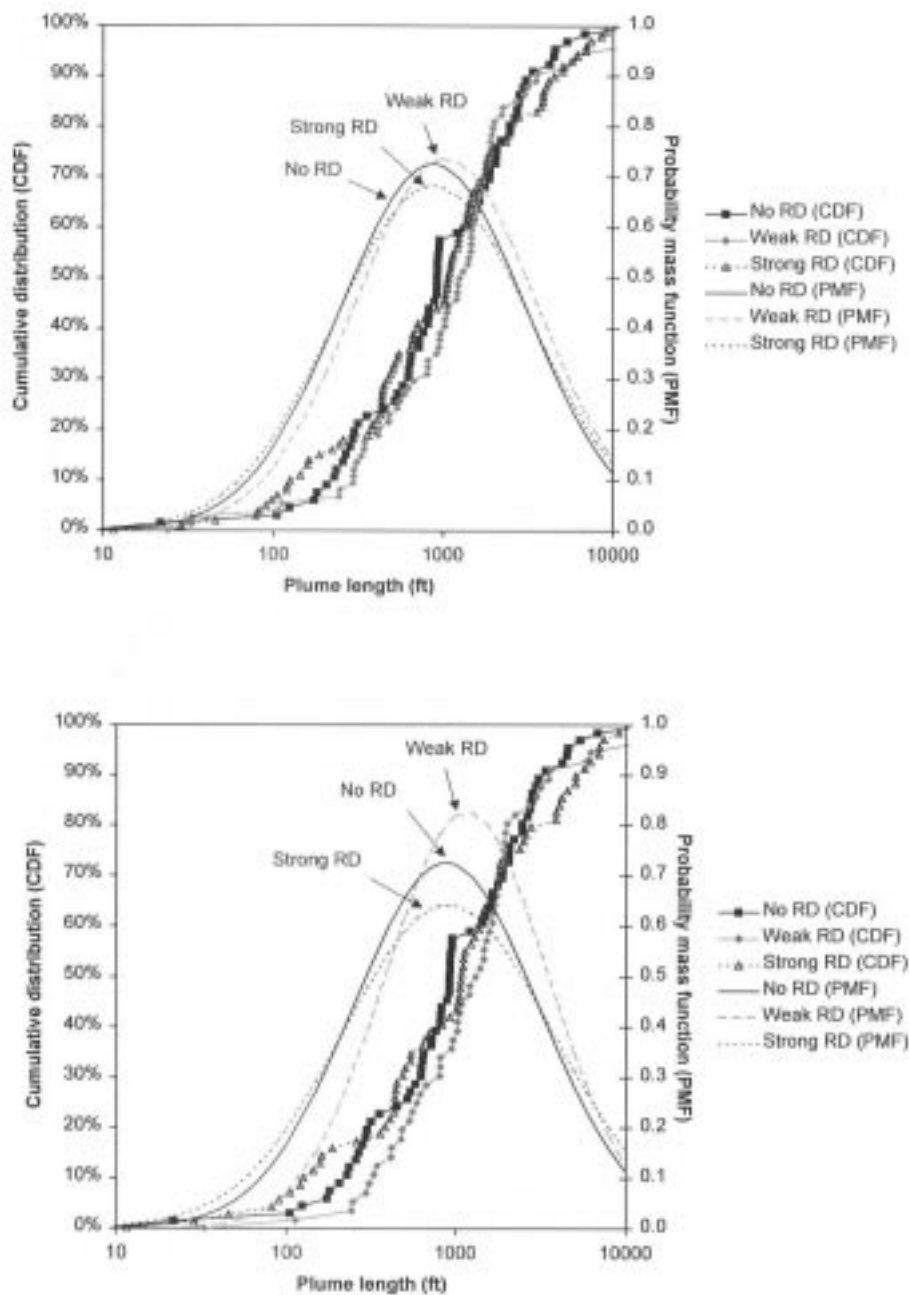


Figure A-6. Cumulative distributions of plumes lengths from sites exhibiting no evidence of reductive dehalogenation, weak evidence, and strong evidence, all CVOCs from each site (top) and CVOCs exclusive of *cis*-1,2-DCE and vinyl chloride daughter products (bottom). Frequency distributions determined by a best fit lognormal distribution model are indicated on the second y-axis.



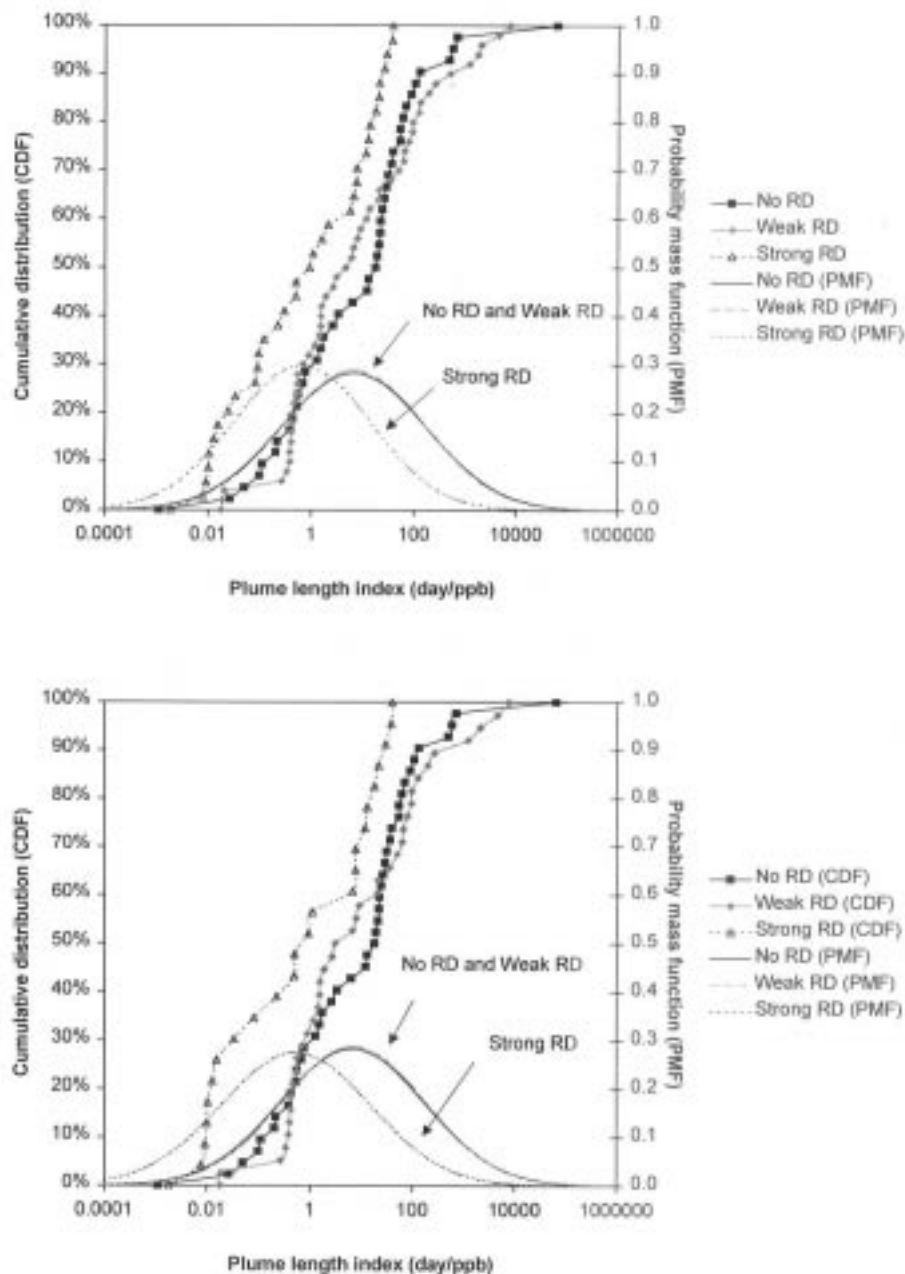


Figure A-7. Cumulative distributions of plumes length indices from sites exhibiting no evidence of reductive dehalogenation, weak evidence, and strong evidence, all CVOCs from each site (top) and CVOCs exclusive of *cis*-1,2-DCE and vinyl chloride daughter products (bottom). Frequency distributions determined by a best fit lognormal distribution model are indicated on the second y-axis.

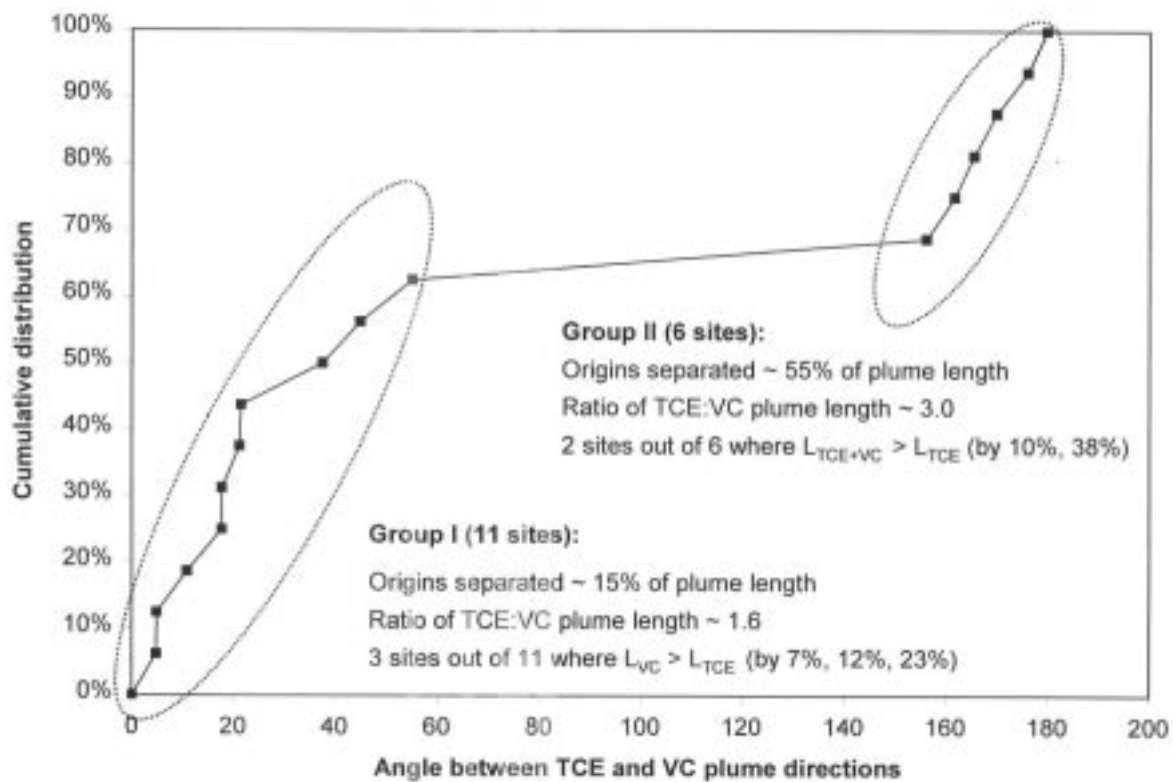


Figure A-8. Cumulative distribution of angles between TCE and vinyl chloride plume directions as interpreted by the plume algorithm

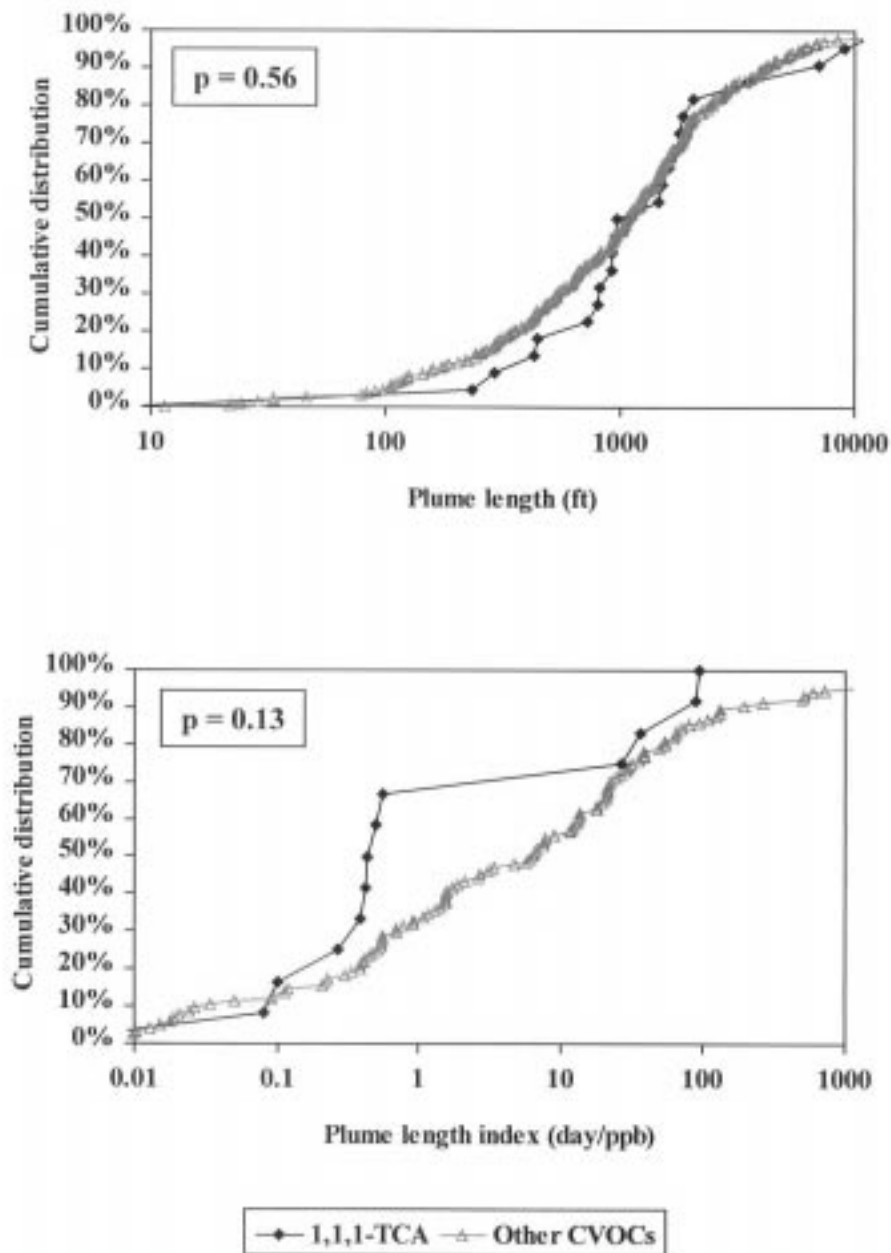
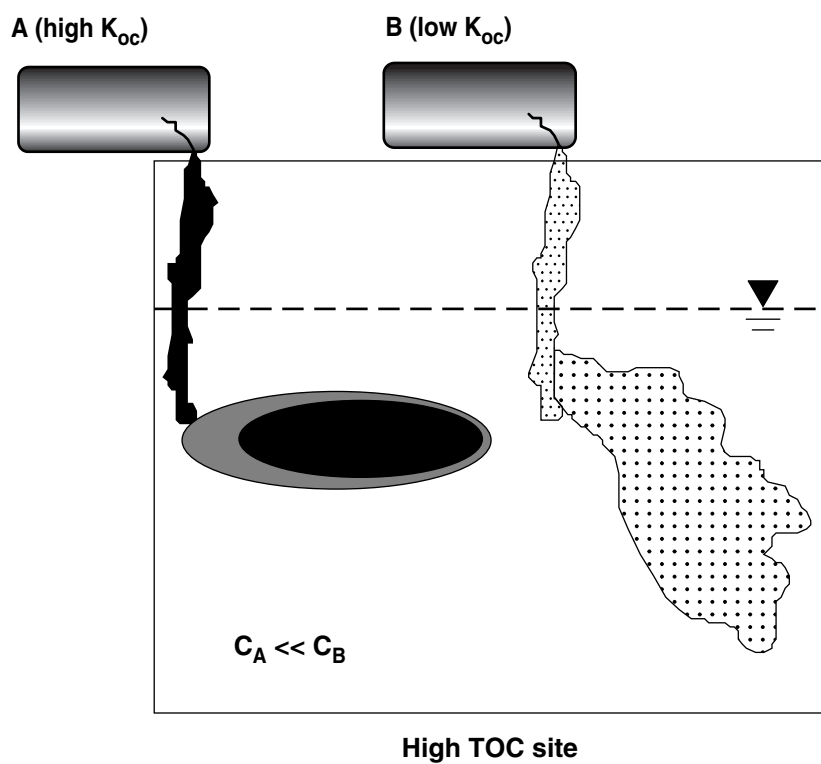
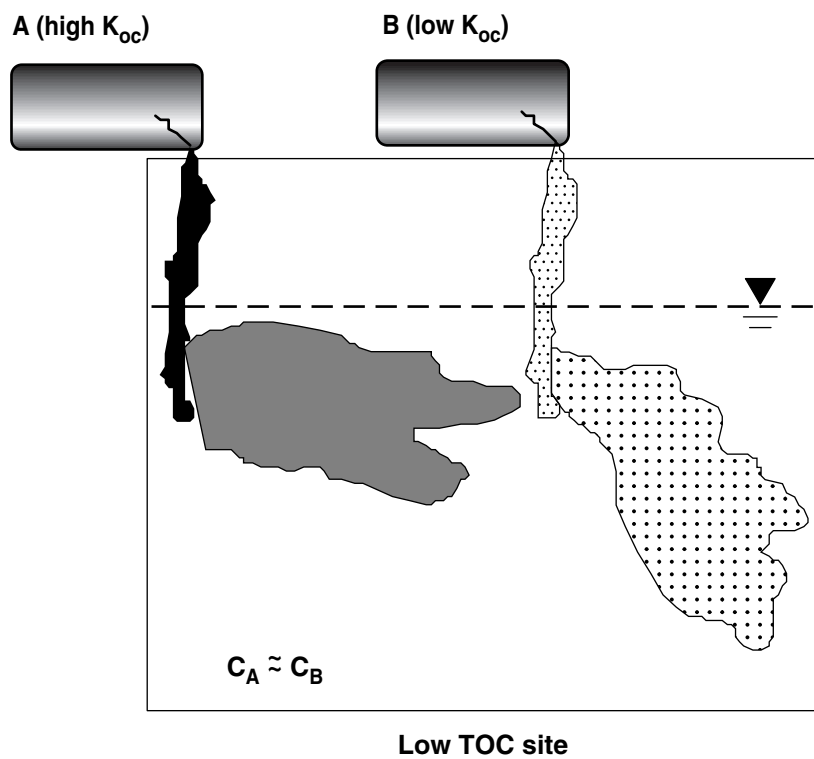


Figure A-9. Cumulative distributions of 1,1,1-TCA plume lengths and those of other CVOCs (top), and distributions of plume length indices (bottom).



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Figure A-10. Idealized release scenarios for CVOCs with low and high organic carbon partitioning coefficients, low organic carbon environment (top) and, high organic carbon environment (bottom).

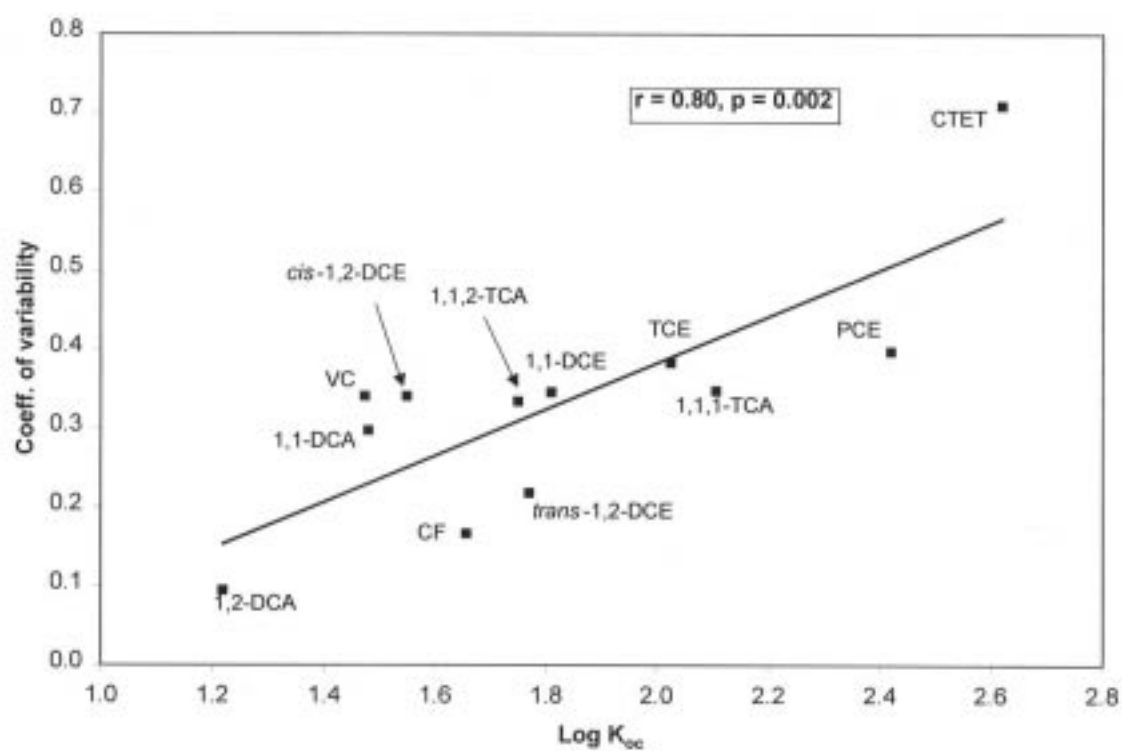
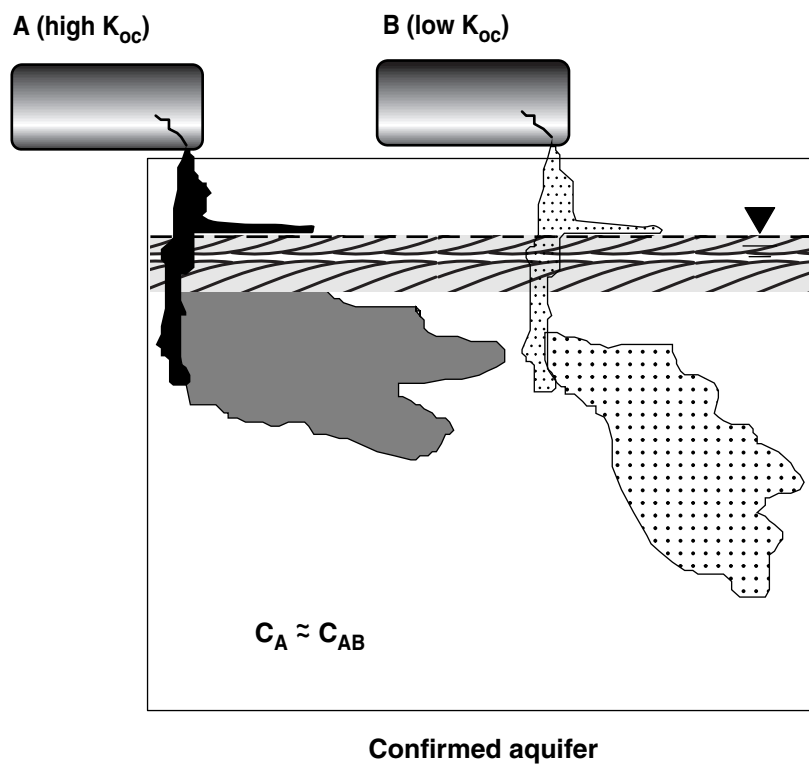
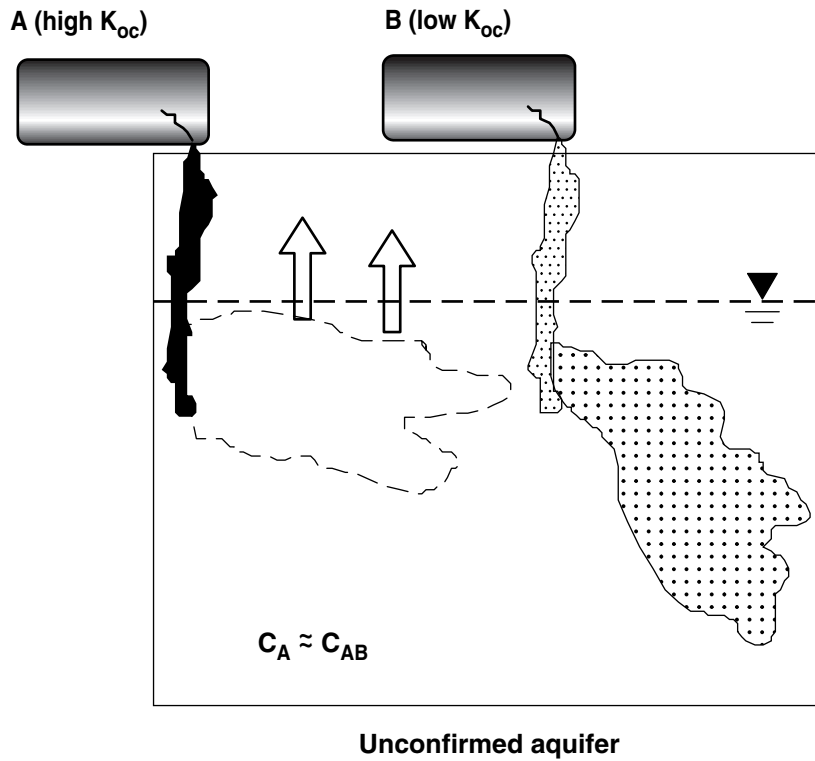


Figure A-11. Relationship between the coefficient of variability in maximum historical concentration between sites and the organic carbon partitioning coefficient for CVOCs represented by six or more plumes.



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Figure A-12. Idealized release scenarios for CVOCs with low and high Henry's constants, confined aquifer (top) and unconfined aquifer (bottom).

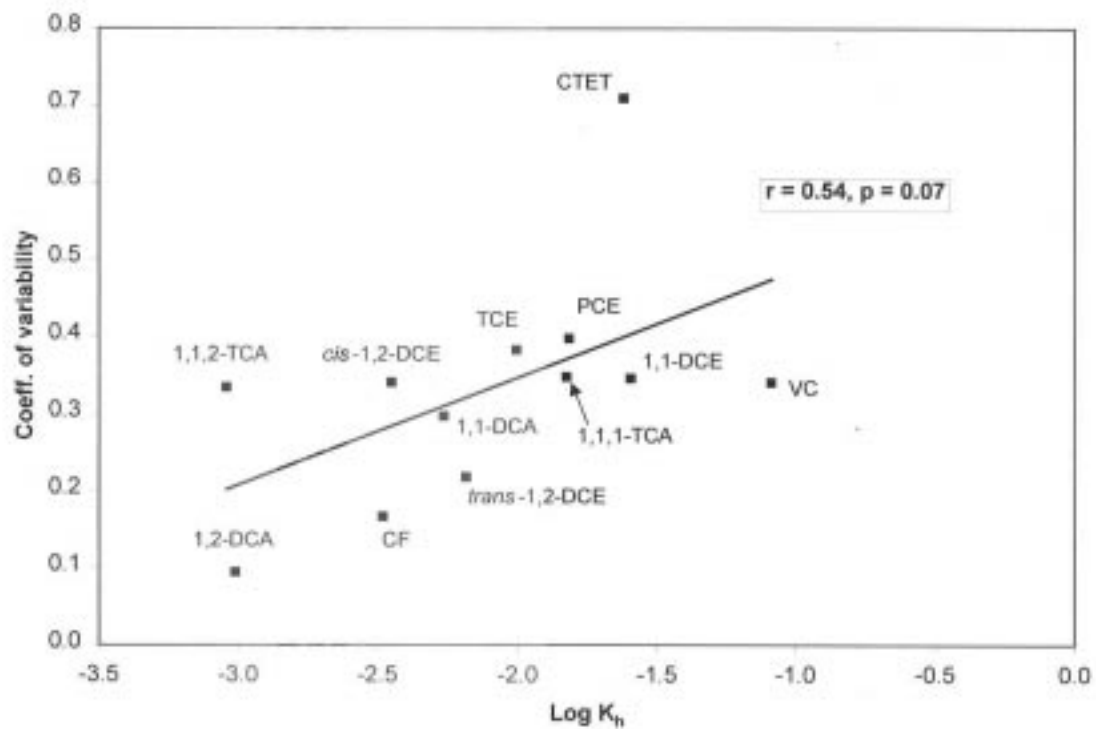


Figure A-13. Relationship between the coefficient of variability in maximum historical concentration between sites and the Henry's constant for CVOCs represented by six or more plumes.

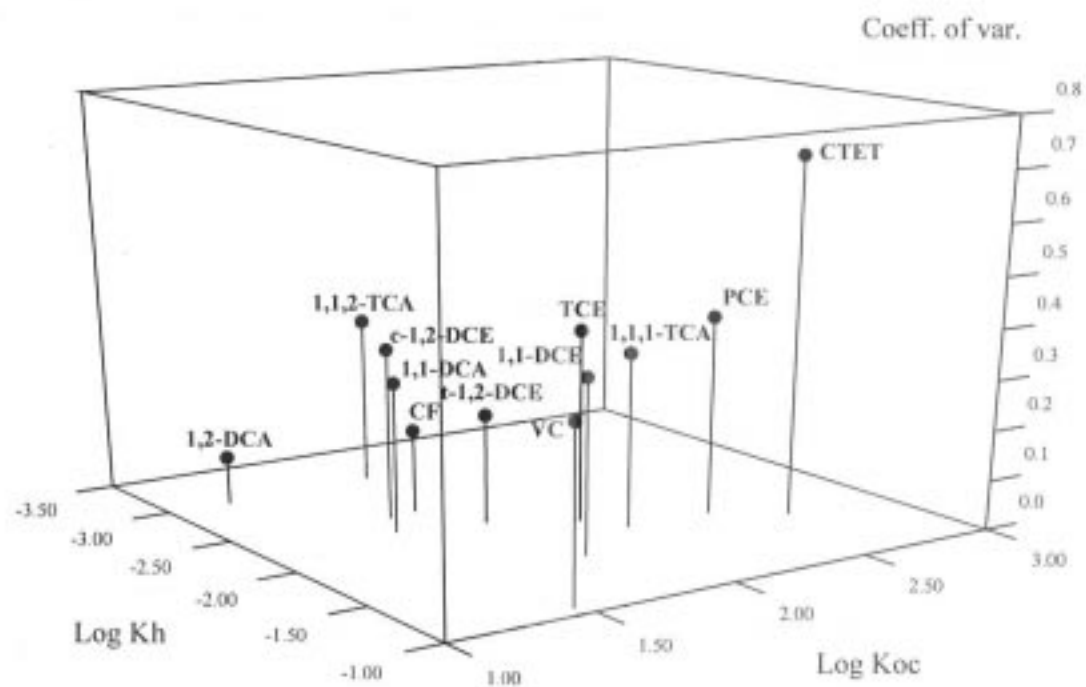


Figure A-14. A three-dimensional scatter plot showing the relationship between coefficient of variability in maximum historical concentration between sites and the organic carbon partitioning coefficient and the Henry's constant for CVOCs represented by six or more plumes.



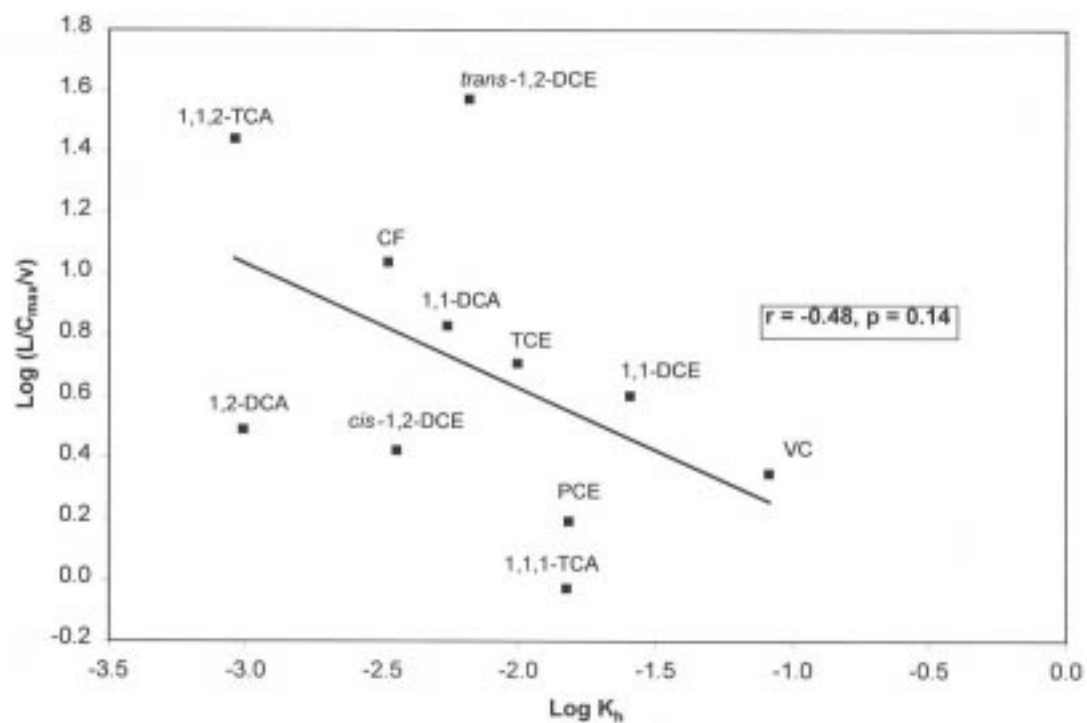


Figure A-15. Relationship between the mean of the log plume length indices and the Henry's constant for CVOCs represented by three or more plumes.



# **Appendix B**

## **Plume Length Algorithm**



## Appendix B

### Plume Length Algorithm

Plume length is the primary plume metric of interest in this study because it reflects the potential of the contaminant to impact nearby receptors such as water supply wells. Furthermore, other important plume metrics, such as the plume rate-of-growth, are necessarily defined in terms of plume length. Nevertheless, plume length is an inherently nebulous concept because of the highly irregular morphology of solute plumes in the subsurface environment, exacerbated through biases created by monitoring well network configurations. Therefore, it is important to establish an objective protocol for the systematic quantification of plume length for each CVOC at each site in the study. It is not possible to accomplish this using interpreted plume contour maps because such maps are not always defined objectively, particularly from site to site among different investigators. Hence, it is preferable to prescribe a plume algorithm to estimate plume lengths directly from CVOC concentration data and well locations at each site.

For the purposes of this study, plume length is defined as the distance from the source area (specifically, the well exhibiting maximum concentration of the CVOC of interest) to the farthest leading edge of the plume at a defined concentration contour (either 10-, 100-, or 1000-parts-per-billion). This definition is two-dimensional in nature; spreading of the plume in the vertical direction is not evaluated due to the limited amount of depth-specific data available, the higher relative importance of plume length, and the complexity of three-dimensional versus two-dimensional modeling. Given a sparse monitoring well network, the distance from the source area to the leading plume edge must be interpolated. Logically, the minimum plume length,  $L_{\min}$ , is constrained by the distance from the well exhibiting the maximum historical CVOC concentration to the furthest down-gradient well exhibiting a concentration higher than the defined contour. Exponential projection of the concentration profile through this well pair can be used to provide an alternative plume length estimate ( $L_{\text{proj}}$ ). However, experience has shown that exponential projection tends to overestimate plume lengths in comparison to visual inspection of plume maps. In practice, the harmonic mean of the constrained minimum plume length and the exponential projected plume length was found to yield the most satisfactory match with observed plume lengths measured from site maps and was thus selected as the plume length ( $L$ ) algorithm for the study:

$$\frac{1}{L} = \frac{1}{2} \left( \frac{1}{L_{\min}} + \frac{1}{L_{\text{proj}}} \right) \quad (\text{Eq. B-1})$$

For each plume, plume length was estimated by year using annually-averaged concentrations in each monitoring well. The maximum historical plume length was then chosen as the plume length for the given CVOC at the site. This takes into account the highest degree of plume delineation as more monitoring wells come on line over time and yet avoids incorporating the effects of remediation activities on plume length in later years.

A comparison of plume lengths taken from site maps with the plume lengths computed using the plume length algorithm is shown in Figure B-1. The concept of plume length as defined in this study was applied in like manner to both the original contaminant CVOCs (e.g., PCE) as well as to probable daughter product compounds (e.g., vinyl chloride). Thus, daughter product plumes lengths were defined with reference to the maximum concentration of the daughter product, rather than to the maximum concentration of the presumed parent product. This strategy was necessary for two reasons:

1. The precise location of the source of a contaminant plume was not known or reported in many instances. Even for a single species, this complicated the task of defining a plume length. For this reason, the location at which the maximum historical concentration was measured provided a systematic, objective basis for defining plume length because: (1) it could always be defined for any plume, and (2) in most instances, the highest concentrations would in all likelihood be encountered in close proximity to the source area. When possible daughter product plumes are introduced, the problem of identifying the source area is even more difficult. At many sites, mixtures of contaminants were released in several locations, making it difficult to associate a daughter product plume with a specific parent product source location. For example, there are 55 TCE plumes and 32 PCE plumes in the data set. Many of these PCE and TCE plumes coexist at individual sites, raising the question of whether or not a *cis*-1,2-DCE or vinyl chloride plume at these sites should be associated with the PCE source or the TCE source. Within the data set, there are instances where either a PCE and/or a TCE plume are not evident and yet a *cis*-1,2-DCE and/or a vinyl chloride plume is present. In such cases, it would be very difficult to measure the daughter product plume length with respect to a parent product source area when the latter cannot be defined. A further potential difficulty is that reductive dehalogenation may take place only locally, so that a small, localized daughter product plume could develop far downgradient of the parent product source area. In such instances, defining a daughter product plume length with respect to the parent product plume origin would yield a non-physical daughter product plume of excessive length. Such a plume length could not be used in multivariate analyses as it would distort the relationships with respect to site variables. For all of these reasons, defining daughter product plume length with respect to the maximum historical concentration of the daughter product compound was the best strategy for preserving objectivity in the analyses. In this way, plume lengths could be defined independently from the type of source responsible for the plume's existence (e.g., DNAPL dissolution, leaching of dissolved a CVOC from the vadose zone, or reductive dehalogenation).
2. For several of the CVOCs included in the study, the original contaminant-daughter product role cannot be unambiguously identified. A well-known example is that of TCE, which certainly exists at many sites as an original contaminant but may also exist as a reductive dehalogenation daughter product of PCE. Chloroform and 1,1-DCA have both been used as solvents in a variety of industrial applications (Pankow et al., 1996) and yet may also be produced as reductive dehalogenation intermediates. 1,1-DCE presents an especially troublesome example, having industrial uses and hence being a possible original contaminant (Montgomery and Welkom, 1990), being produced as a reductive dehalogenation product of PCE and TCE, and being produced as an abiotic transformation product of 1,1,1-TCA.

## References

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- Pankow, J. F., S. Feenstra, J. A. Cherry, and M. C. Ryan (1996), “Dense chlorinated solvents in groundwater: Background and history of the problem,” in *Dense Chlorinated Solvents*, Pankow, J. F., and J. A. Cherry, Eds. (Waterloo Press, Portland, Oreg.), pp. 1–52.

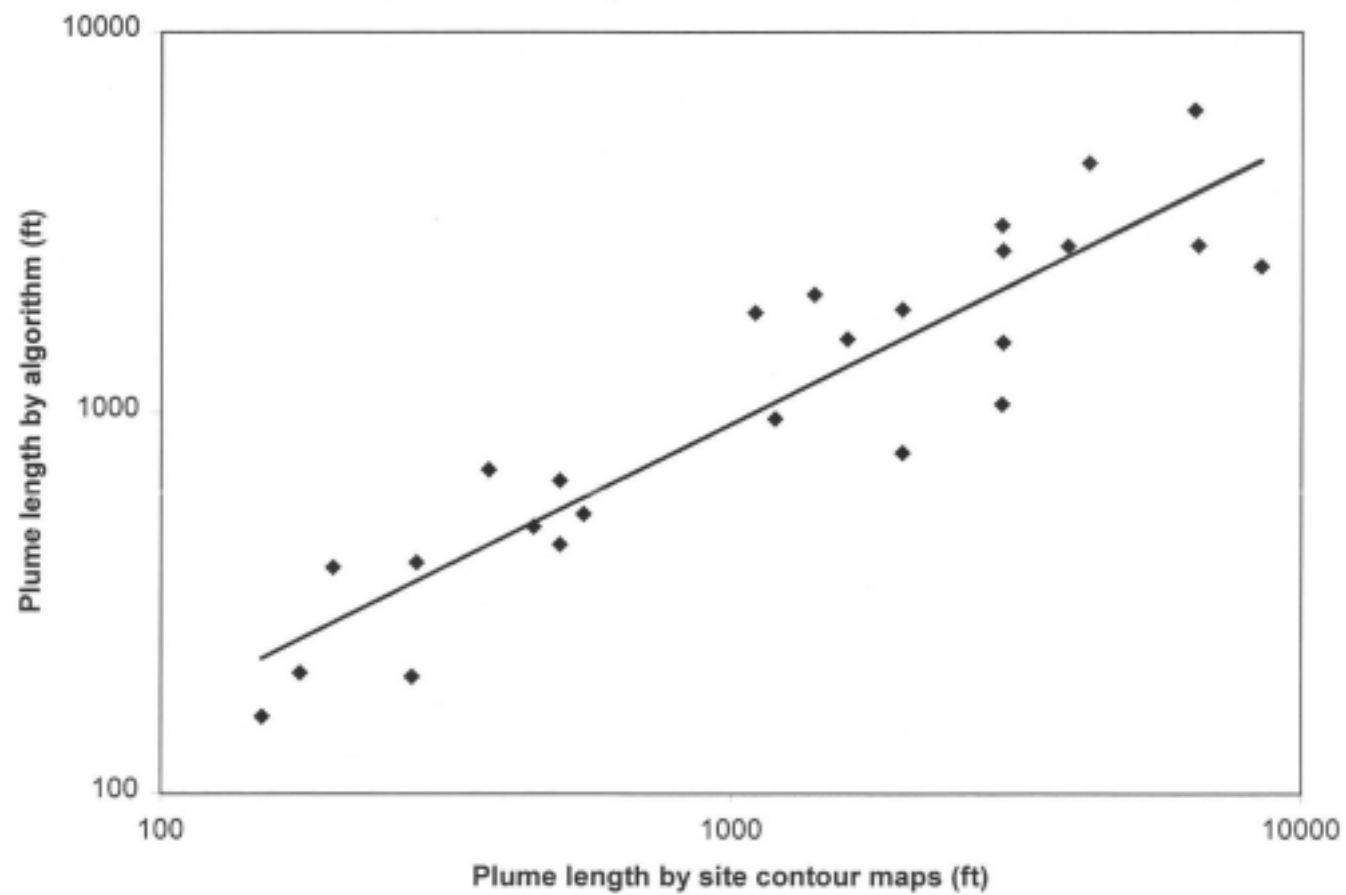


Figure B-1. Comparison of plume-algorithm-generated plume lengths with those interpreted from plume maps provided in individual site reports (as delineated by the 10-ppb contour).



## **Appendix C**

### **Application of a General Linear Model (GLM) to the Analysis of CVOC Historical Case Data**



## Appendix C

# Application of a General Linear Model (GLM) and an Analysis of Covariance (ANCOVA)

### C.1. Background

As stated in Appendix A, it is presumed that plume length will co-vary with other important variables, such as the strength of the source term or groundwater velocity, in addition to reductive dehalogenation. In this case, the form of the general linear model corresponds to an analysis of covariance or ANCOVA (Steel and Torrie, 1980), where the variable referred to as “EVIDENCE” is considered the treatment effect in the presence of other modeled covariates. Note, incidentally, that this statistical analysis is based on observational and not experimental data. Plumes were not randomly assigned to the treatment conditions.

It is important to define the scope of inference regarding the conclusions of these statistical analyses. To reliably generalize the interpretation of these results to the entire population of CVOC plumes in the United States, a randomly selected sample of  $N$  plumes from the identified or target population would have to be sampled. This was certainly not the case in this study. In fact, defining this population may be a cost-prohibitive exercise. Instead, the more practical strategy has been to identify and obtain data on CVOC plumes from a broad geographic area with the intent to secure a representative sample. The conclusions under the theoretical scope of inference can be made with confidence and quantifiable uncertainty, but practicality necessitates settling for reasonable reliability instead.

### C.2. General Linear Model Description and Results

In order to perform analysis of covariance (ANCOVA) by a general linear model for log plume length, three indicator or dummy variables were first created:

ind1 = 1, if EVIDENCE is "STRONG"  
0, otherwise  
ind2 = 1, if EVIDENCE is "WEAK"  
0, otherwise  
ind3 = 1, if EVIDENCE is "NONE"  
0, otherwise

In addition, the two covariates ( $\log(\text{max. conc.})$  and  $\log(\text{meanV})$ , where V is groundwater velocity) were multiplied by each of the indicator variables which produced the following new variables defined as:

$$XC_1 = \begin{cases} \log(\text{max. conc.}), & \text{if EVIDENCE is "STRONG"} \\ 0, & \text{otherwise} \end{cases}$$

$$XC_2 = \begin{cases} \log(\text{max. conc.}), & \text{if EVIDENCE is "WEAK"} \\ 0, & \text{otherwise} \end{cases}$$

$$XC_3 = \begin{cases} \log(\text{max. conc.}), & \text{if EVIDENCE is "NONE"} \\ 0, & \text{otherwise} \end{cases}$$

and,

$$XV_1 = \begin{cases} \log(\text{meanV}), & \text{if EVIDENCE is "STRONG"} \\ 0, & \text{otherwise} \end{cases}$$

$$XV_2 = \begin{cases} \log(\text{meanV}), & \text{if EVIDENCE is "WEAK"} \\ 0, & \text{otherwise} \end{cases}$$

$$XV_3 = \begin{cases} \log(\text{meanV}), & \text{if EVIDENCE is "NONE"} \\ 0, & \text{otherwise} \end{cases}$$

Therefore, this system of coding for the general linear model, allows us to fit a “full model”

$$Y_i = \beta_{01} \text{ind}_{1i} + \beta_{02} \text{ind}_{2i} + \beta_{03} \text{ind}_{3i} + \beta_{11} XC_{1i} + \beta_{12} XC_{2i} + \beta_{13} XC_{3i} + \beta_{21} XV_{1i} + \beta_{22} XV_{2i} + \beta_{23} XV_{3i} + \varepsilon_i \quad (\text{Eq. C-1})$$

and a “reduced model”

$$Y_i = \beta_{01} \text{ind}_{1i} + \beta_{02} \text{ind}_{2i} + \beta_{03} \text{ind}_{3i} + \beta_1 \log(\text{max. conc.}) + \beta_2 \log(\text{meanV}) + \varepsilon_i \quad (\text{Eq. C-2})$$

The full model (Eqn. C-1) allows the bivariate linear regressions of the log of plume length (Y) on the log of maximum concentration and the log of mean groundwater velocity to be fit separately for each level of the main effect, EVIDENCE. For example,  $Y_{ji}$ , the  $i^{\text{th}}$  measurement of log plume length for plumes where  $j = 1$  representing STRONG evidence of reductive dehalogenation, can be described by the sub-model:

$$Y_{1i} = \beta_{01} \text{ind}_{1i} + \beta_{11} XC_{1i} + \beta_{11} XV_{1i} + \varepsilon_i \quad (\text{Eq. C-3})$$

Similar sub-models can be identified for each of the other two levels of EVIDENCE (i.e., WEAK and NONE). This means that the slope parameters of the regression relationships described above for each level of EVIDENCE are free to vary, viz., they are heterogeneous.

This model is tantamount to a completely specified model for an ANCOVA. The advantage of fitting Eqn. C-1 is that all parameters among all levels of EVIDENCE can be fit simultaneously.

By the method known as reduction sum of squares (Searle 1987), we can test the hypothesis that any  $Y_{ji}$  can be described simply as a function of the intercept parameter ( $\alpha_{0j}$ ) for the  $j^{\text{th}}$  level of EVIDENCE and common slope parameter for each covariate ( $\alpha_{1j}, \alpha_{2j}$ ). This hypothesis assumes that the slope parameters among the covariates are homogeneous, ( $\alpha_{k1} = \alpha_{k2} = \alpha_{k3}, k=1,2$ ), for the  $k^{\text{th}}$  covariate.

We then calculate the statistic:

$$F = \frac{(\text{SSE}_{\text{reduced model}} - \text{SSE}_{\text{full model}}) / \text{no. of parameters}}{\text{MSE}_{\text{full model}}} \quad (\text{Eq. C-4})$$

where SSE is the error sum of squares for each of the two models.

The statistic in Eq. C-4 is distributed as a  $F_{n1,n2}$  distribution with numerator degrees of freedom ( $n1$ ) equal to difference ( $\Delta$ ) in the number of parameters specified in the full and reduced models, and the denominator degrees of freedom ( $n2$ ) equal to that corresponding to the mean squared error (MSE) of the full model.

From the analysis results given in Tables C-1a through C-1e and C-2a through C-2e, performed using the JMP (version 3.2.1) software from SAS Institute,

$$F_{4,120} = \frac{(26.540697 - 26.031044) / 4}{.216925} = 0.587$$

If the homogeneous slopes hypothesis is true, we would expect to obtain an F statistic as large or larger than 0.587 approximately 70% of the time (i.e.,  $p = 0.672$ ). We may conclude that there is insufficient evidence for rejecting this hypothesis with a power for detecting slope heterogeneity, if there was any, about 98% of the time.

Furthermore, a test for whether or not plumes with STRONG evidence of reductive dehalogenation are shorter than plumes with either WEAK or no (NONE) evidence is a matter of comparing the intercept parameters ( $\alpha_{0j}$ ) in the reduced model. Specifically, we can test whether or not  $\alpha_{01} - \alpha_{0j} < 0$  [for  $j=2$ (WEAK),  $3$ (NONE)]; this can be accomplished by performing a standard ANCOVA, again using the JMP software, with corresponding paired comparisons among the least squares means presented in Tables C-3a through C-3h, Tables C-4a through C-4h, and Plots C-3c through C-4f.

### C.3. ANCOVA Results

A plot of the CVOC plume length means on the log scale for all CVOCs with six or more recorded plumes is shown on Figure C-1. In order to justify the use of the entire data set in the subsequent statistical model, it is important to demonstrate that there are no statistically significant differences in plume length among the several CVOC species. The overall mean plume length is shown on Figure C-1 as the horizontal line crossing the entire plot. The center line within each diamond indicates the mean plume length for that CVOC species the top and

bottom of the diamond indicates the upper and lower 95% confidence limits, respectively, using a pooled estimate of plume length variance among all plumes. The diameter of the comparison circles to the right of the means plot is proportional to the standard deviation of plume lengths on the log scale. The angle formed by two tangent lines between overlapping circles is an indication of the statistical significance of that comparison. If the angle formed is  $< 90^\circ$  then we may conclude that the given pair of CVOCs is statistically different with a 5% chance or less of error ( $p < 0.05$ ). These circles suggest little evidence for a practical difference in plume length among CVOCs. An analysis of variance (ANOVA) (Steel and Torrie, 1980) test also indicates that there is indeed insufficient evidence for a statistically significant difference among CVOC plume lengths ( $p = 0.14$ ) at the 5% level (i.e., the error rate for false positive conclusions).

One other important assumption prior to conducting an ANCOVA is to test the assumption that the log of plume lengths is normally distributed. A histogram of these plume lengths on the log scale, a box-and-whisker plot, and a normal quantile plot are all shown on Figure C-2. Each plot is designed to show the strength of the evidence for the normality assumption. A theoretical normal (bell) curve is superimposed on the histogram whose mean is the sample mean of the plume length logarithms. The box-and-whisker plot shows the quantiles where the horizontal bar is the median (50th percentile) and the top and bottom of the box are the 75th and 25th percentiles, respectively. The diamond indicates the mean, which, if the sample data are normally distributed, should be nearly identical to the median. The normal quantile plot shows the theoretical quantile of the data as standard normal deviates on the abscissa and the actual values (logs) of plume lengths on the ordinate axis. If the data derive from a normal distribution, the data would all fall along a straight line. This plot indicates that the shortest plume lengths are shorter than expected under the lognormal probability distribution model. Furthermore, an inference test of normality (Shapiro-Wilk W-Test) indicates a statistically significant departure from this assumption ( $p = 0.0004$ ).

Given the results of the normality test, an additional ANCOVA was performed on the ranks of the plume length as an equivalent non-parametric test (Conover, 1980). This test again indicated no significant difference in plume lengths among CVOC species ( $p = 0.40$ ).

The relationship between the plume length and each of the two covariates, maximum concentration and mean velocity, respectively, are shown on the log scale on Figures C-3 and C-4. Three difference linear regression lines are also shown in each plot, one for a separate fit for each category of EVIDENCE. With the exception of plumes showing strong evidence of reduction dehalogenation in Figure C-4, the slopes of these relationships are very similar. The aim of the subsequent GLM was to test, simultaneously, whether these slopes are can be considered equal to one another by a comparative reduction in the error sum of squares between two models, one which assumes equal slopes and one which does not (Searle, 1987). If so, the ANCOVA test for differences in mean plume lengths between evidence categories is tantamount to comparing the intercepts in Figures C-3 and C-4. The results of this analysis are provided in the Appendix A. The GLM results indicated insufficient evidence for concluding that these slopes are different ( $p = 0.672$ ). The resulting and simplified ANCOVA model justifiably contains only a main effect term for EVIDENCE and the two covariates with a common slope parameter for each covariate. The ANCOVA results indicated a significant and positive relationship between plume length and only two covariates, maximum concentration ( $p < 0.001$ ) and mean velocity ( $p = 0.008$ ). In this analysis, there were 129 of the 243 plumes described earlier for which complete data for EVIDENCE and covariates were measured.

The least squares mean plume lengths for each category of EVIDENCE on the original and log scale resulting from the ANCOVA are presented on Table C-2. Least squares mean plume lengths are sample means adjusted for the relationships with the covariates. As indicated on the table, plumes with strong evidence of reductive dehalogenation are shorter than plume lengths with either weak or no evidence. The ANCOVA results indicate that these two paired comparisons of plume length means are statistically significant,  $p = 0.004$  and  $p = 0.003$ , respectively.

An ANCOVA was also performed on the ranks of plume lengths as a corresponding equivalent nonparametric test. The conclusions were similar, viz., that a significant and positive relationship exists between plume length and only two covariates, maximum concentration ( $p < 0.0001$ ) and mean velocity ( $p = 0.0014$ ), and that the mean plume lengths are significantly shorter when there is strong evidence of reductive dehalogenation as compared to plumes with weak ( $p = 0.001$ ) or no evidence ( $p = 0.002$ ).

A plot of the cumulative distribution of the residuals from the ANCOVA model displayed separately for each category or level of EVIDENCE, in order from smallest to largest, is presented on Figure C-5. A residual is the difference between the fitted value from the model and the actual value. Residuals are normally distributed with a mean equal to zero. This means that there are positive residuals (i.e., plumes longer than expected by the model) and negative residuals (i.e., plumes shorter than expected by the model). Consequently, accumulating the values of residuals, from smallest to largest, will yield an inverted parabola shape to the cumulative distribution function. If there were no difference between the levels of EVIDENCE, these inverted parabolas would overlay each other. Instead, not only are they separated but there are different minimum values for each.

The smallest minimum value in Figure C-5, occurs among residuals for those plumes with the strongest evidence of reductive dehalogenation. This indicates that there were shorter plumes (i.e., more negative residuals) in this level of EVIDENCE than in any other. The maximum for each cumulative distribution in Figure C-5, is zero because the sum of the residuals is zero. These maximums occur at a different value of order corresponding to the samples size or number of plumes in each level of EVIDENCE.

As in the previous data analysis by cumulative distribution of plume length indices (see Appendix A), the cumulative distribution of residuals from an ANCOVA model corroborates the finding that the shortest CVOC plumes are associated with the strongest evidence of reductive dehalogenation.

An additional ANCOVA was performed on a subset of the CVOC data that excluded “daughter” plumes. Such plumes are derived from the breakdown of other CVOC species and were used to define the EVIDENCE category. This analysis is an attempt to eliminate a suspected data bias or over representation of shorter plumes in the larger data set. Therefore, data from sixteen cis-1,2-DCE, and seven vinyl chloride plumes were deleted from the previous data set containing 129 plumes with complete information for all variables in the statistical model. A second ANCOVA was then performed.

The analysis of the subsequent 106 CVOC plumes showed that both maximum concentration and mean velocity were still statistically important ( $p = 0.002$  and  $p = 0.083$ , respectively) in explaining the variation in the log of plume length. However, mean velocity was substantially

less helpful than maximum concentration, contrary to the earlier ANCOVA results which used all of the CVOC plumes (see Tables C-3 and C-4). But having accounted for the variation in log plume length due to these two covariates, we may still conclude with confidence that plumes exhibiting strong EVIDENCE of reductive dehalogenation are significantly shorter than plumes with either weak or no EVIDENCE ( $p = 0.003$  and  $p = 0.004$ , respectively).

Table C-3 shows that the statistical bias-corrected (Gilbert 1987) estimates of the median plume length (with or without the daughter plumes), when there is strong EVIDENCE of reductive dehalogenation, is about half as long as a plume showing either weak or no EVIDENCE.

## References

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- Gilbert, R. O. (1987), Statistical Methods for Environmental Pollution Monitoring, Van Nostrand Reinhold Co., New York.
- Searle, S. R. (1987), Linear Models for Unbalanced Data (Wiley, New York).
- Steel, R. G. D., and Torrie, J. H. (1980), Principles and Procedures of Statistics: A Biometrical Approach (2<sup>nd</sup> Edition), McGraw-Hill Book Co., New York.



## Tables C-1.

**Table C-1a. Response: Log (Length) Summary of Fit.**

Statistical parameters	Statistical results
R Square	0.197504
R Square (adjusted)	0.144004
Root Mean Square Error	0.465752
Mean of Response	2.929986
Observations (or sum of weights)	129

**Table C-1b. Parameter estimates.**

Term	Estimate	Std error	t ratio	Prob >  t
Intercept	Zeroed	0	0	–
ind1	2.0703486	0.273666	7.57	<0.0001
ind2	2.8842836	0.245101	11.77	<0.0001
ind3	2.593284	0.211894	12.24	<0.0001
XC1	0.1252731	0.075691	1.66	0.1005
XC2	0.0964387	0.062325	1.55	0.1244
XC3	0.170673	0.065222	2.62	0.0100
XV1	0.5525953	0.242685	2.28	0.0246
XV2	-0.12301	0.076677	-1.60	0.1113
XV3	-0.106314	0.091102	-1.17	0.2455

**Table C-1c. Effect test.**

Source	Nparm	DF	Sum of squares	F ratio	Prob > F
ind1	1	1	12.415234	57.2327	<0.0001
ind2	1	1	30.039765	138.4797	<0.0001
ind3	1	1	32.491845	149.7835	<0.0001
XC1	1	1	0.594207	2.7392	0.1005
XC2	1	1	0.519386	2.3943	0.1244
XC3	1	1	1.485411	6.8476	0.0100
XV1	1	1	1.124702	5.1847	0.0246
XV2	1	1	0.558285	2.5736	0.1113
XV3	1	1	0.295418	1.3618	0.2455

**Table C-1d. Whole model test - Analysis of variance.**

Source	DF	Sum of squares	Mean square	F ratio
Model	8	6.406547	0.800818	3.6917
Error	120	26.031044	0.216925	Prob > F
C Total	128	32.437591	–	0.0007

Tested against reduced model: Y = mean.

**Table C-1e. Whole model test – Power.**

Alpha	Sigma	Delta	Number	Power
0.0500	0.465752	0.222852	129	0.9821

## Tables C-2

**Table C-2a. Response: Log(length) summary of fit.**

Statistical parameters	Statistical results
R Square	0.181792
R Square (adjusted)	0.155398
Root Mean Square Error	0.462642
Mean of Response	2.929986
Observations (or sum of weights)	129

**Table C-2b. Parameter estimates.**

Term	Estimate	Std error	t ratio	Prob >  t
Intercept	Zeroed	0	0	–
ind1	2.3384006	0.141013	16.58	<0.0001
ind2	2.6579117	0.139423	19.06	<0.0001
ind3	2.6539975	0.130973	20.26	<0.0001
log(Max. conc.)	0.1432315	0.038348	3.74	0.0003
log(Mean V)	0.1039279	0.038225	2.72	0.0075

Max. conc. = maximum concentration.

**Table C-2c. Effect test.**

Source	Nparm	DF	Sum of squares	F ratio	Prob > F
ind1	1	1	58.859002	274.9934	<0.0001
ind2	1	1	77.785787	363.4207	<0.0001
ind3	1	1	87.887664	410.6173	<0.0001
log(Max. conc.)	1	1	2.985910	13.9504	0.0003
log(Mean V)	1	1	1.582174	7.3920	0.0075

Max. conc. = maximum concentration.

**Table C-2d. Whole model test - Analysis of variance.**

Source	DF	Sum of squares	Mean square	F ratio
Model	4	5.896894	1.47422	6.8877
Error	124	26.540697	0.21404	Prob > F
C Total	128	32.437591	–	<0.0001

Tested against reduced model: Y = mean.

**Table C-2e. Whole model test – Power.**

Alpha	Sigma	Delta	Number	Power
0.0500	0.462642	0.213804	129	0.9928

## Tables and Plots C-3

### ANCOVA Results - All CVOC Plumes

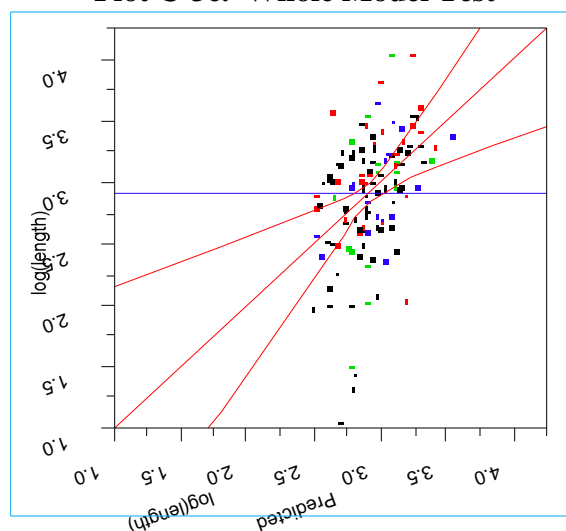
**Table C-3a. Response: Log(length) summary of fit.**

Statistical parameters	Statistical results
R Square	0.181792
R Square (adjusted)	0.155398
Root Mean Square Error	0.462642
Mean of Response	2.929986
Observations (or Sum of weights)	129

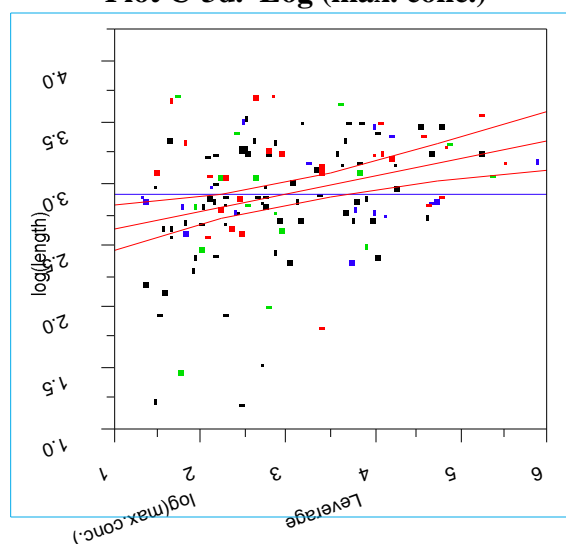
**Table C-3b. Effect test.**

Source	Nparm	DF	Sum of squares	F ratio	Prob > F
log (Max. conc.)	1	1	2.9859101	13.9504	0.0003
log (Mean V)	1	1	1.5821737	7.3920	0.0075
Evidence	2	2	2.4974348	5.8341	0.0038

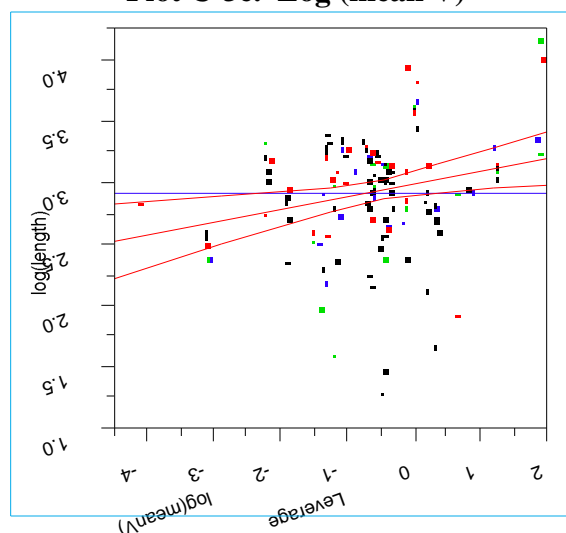
Max. conc. = maximum concentration.

**Plot C-3c. Whole Model Test****Table C-3c. Whole model test - Analysis of variance.**

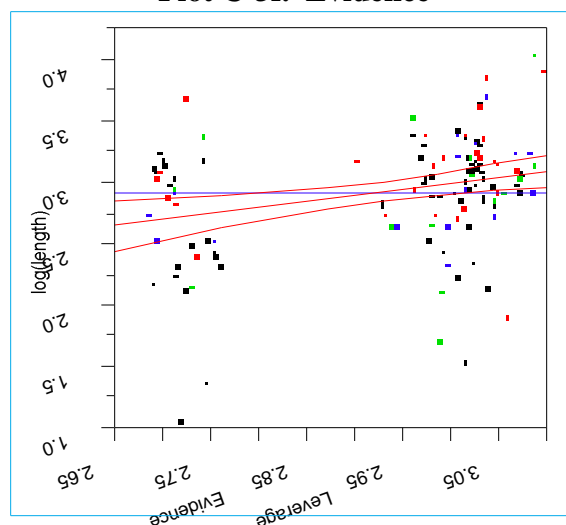
Source	DF	Sum of squares	Mean square	F ratio
Model	4	5.896894	1.47422	6.8877
Error	124	26.540697	0.21404	Prob > F
C Total	128	32.437591	—	<.0001

**Plot C-3d. Log (max. conc.)****Table C-3d. Effect test - Log (max. conc.).**

Sum of squares	F ratio	DF	Prob > F
2.9859101	13.9504	1	0.0003

**Plot C-3e. Log (mean V)****Table C-3e. Effect test - Log (mean V).**

Sum of squares	F ratio	DF	Prob > F
1.5821737	7.3920	1	0.0075

**Plot C-3f. Evidence****Table C-3f. Effect test - Evidence.**

Sum of squares	F ratio	DF	Prob > F
2.4974348	5.8341	2	0.0038

**Table C-3g. Least squares means – Evidence.**

<b>Level</b>	<b>Least sq mean</b>	<b>Std error</b>	<b>Mean</b>
NONE	3.018958411	0.0726928309	2.98939
STRONG	2.703361502	0.0778543976	2.75946
WEAK	3.022872630	0.0659426758	3.00595

**Table C-3h. Contrast – Evidence.**

<b>Variables</b>	<b>Result</b>	<b>Result</b>
NONE	-1	0
STRONG	1	1
WEAK	0	-1
Estimate	-0.316	-0.32
Std Error	0.1068	0.1037
t Ratio	-2.955	-3.08
Prob>   t	0.0037	0.0026
SS	1.8691	2.0303

<b>Statistical parameters</b>	<b>Statistical results</b>
Sum of Squares	2.4974347715
Numerator DF	2
F Ratio	5.8340953965
Prob > F	0.0037888412



## Tables and Plots C-4

### ANCOVA Results: Without CVOC daughter plumes

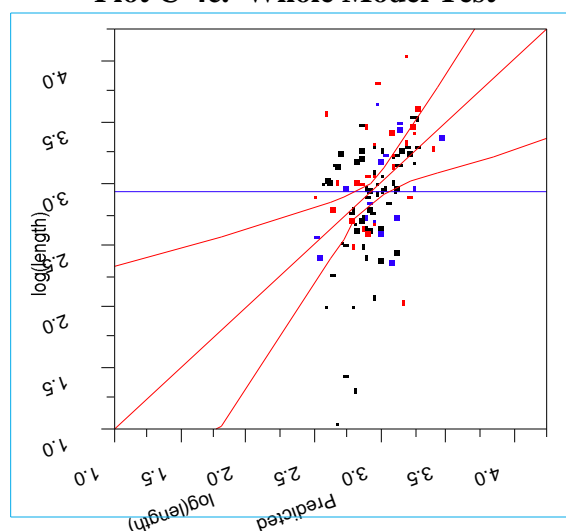
**Table C-4a. Response: Log(length) summary of fit.**

Statistical parameters	Statistical results
R Square	0.175685
R Square (adjusted)	0.143039
Root Mean Square Error	0.449819
Mean of Response	2.944213
Observations (or Sum of weights)	106

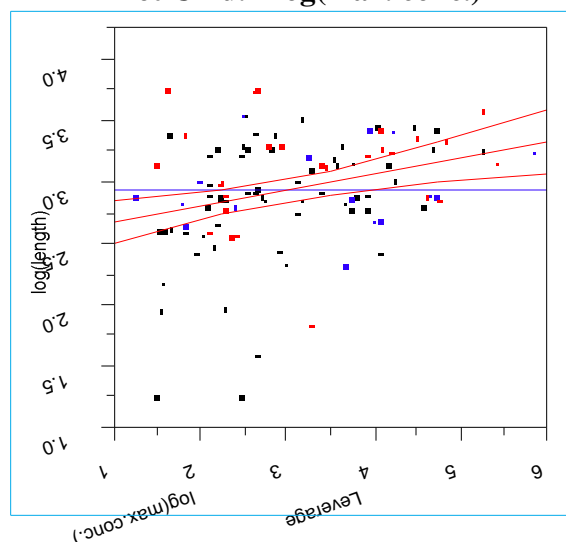
**Table C-4b. Effect test.**

Source	Nparm	DF	Sum of squares	F ratio	Prob > F
log(max. conc.)	1	1	2.0757387	10.2588	0.0018
log(mean V)	1	1	0.6184906	3.0567	0.0834
Evidence	2	2	2.2501787	5.5605	0.0051

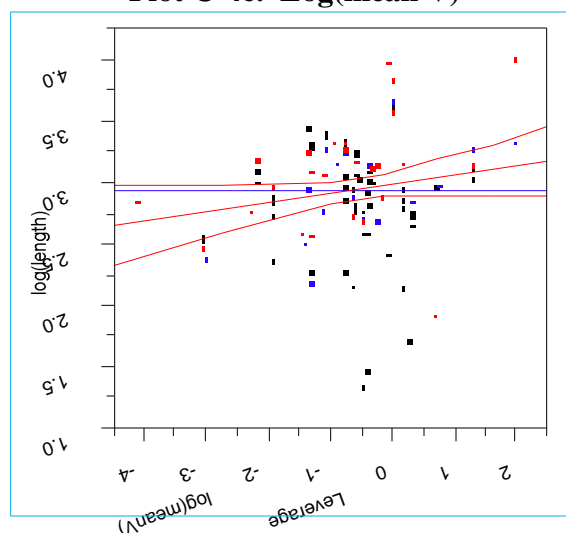
Max. conc. = maximum concentration.

**Plot C-4c. Whole Model Test****Table C-4c. Whole model test - Analysis of variance.**

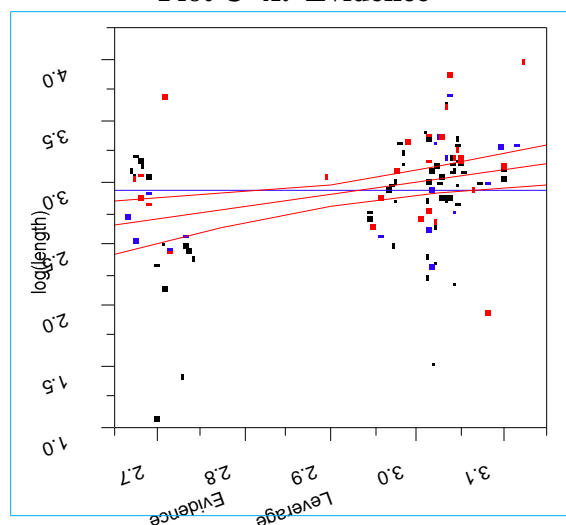
Source	DF	Sum of squares	Mean square	F ratio
Model	4	4.355518	1.08888	5.3815
Error	101	20.436047	0.20234	Prob > F
C Total	105	24.791565	—	0.0006

**Plot C-4d. Log(max. conc.)****Table C-4d. Effect test - Log(maximum concentration).**

Sum of squares	F ratio	DF	Prob > F
2.0757387	10.2588	1	0.0018

**Plot C-4e. Log(mean V)****Table C-4e. Effect test – Log (mean V).**

Sum of squares	F ratio	DF	Prob > F
0.61849063	3.0567	1	0.0834

**Plot C-4f. Evidence****Table C-4f. Effect test – Evidence.**

Sum of squares	F ratio	DF	Prob > F
2.2501787	5.5605	2	0.0051

**Table C-4g. Least Squares Means – Evidence.**

<b>Level</b>	<b>Least sq mean</b>	<b>Std error</b>	<b>Mean</b>
NONE	3.016290076	0.0708913245	2.98939
STRONG	2.680907406	0.0903285548	2.72666
WEAK	3.043977628	0.0738156225	3.04176

**Table C-4h. Contrast – Evidence.**

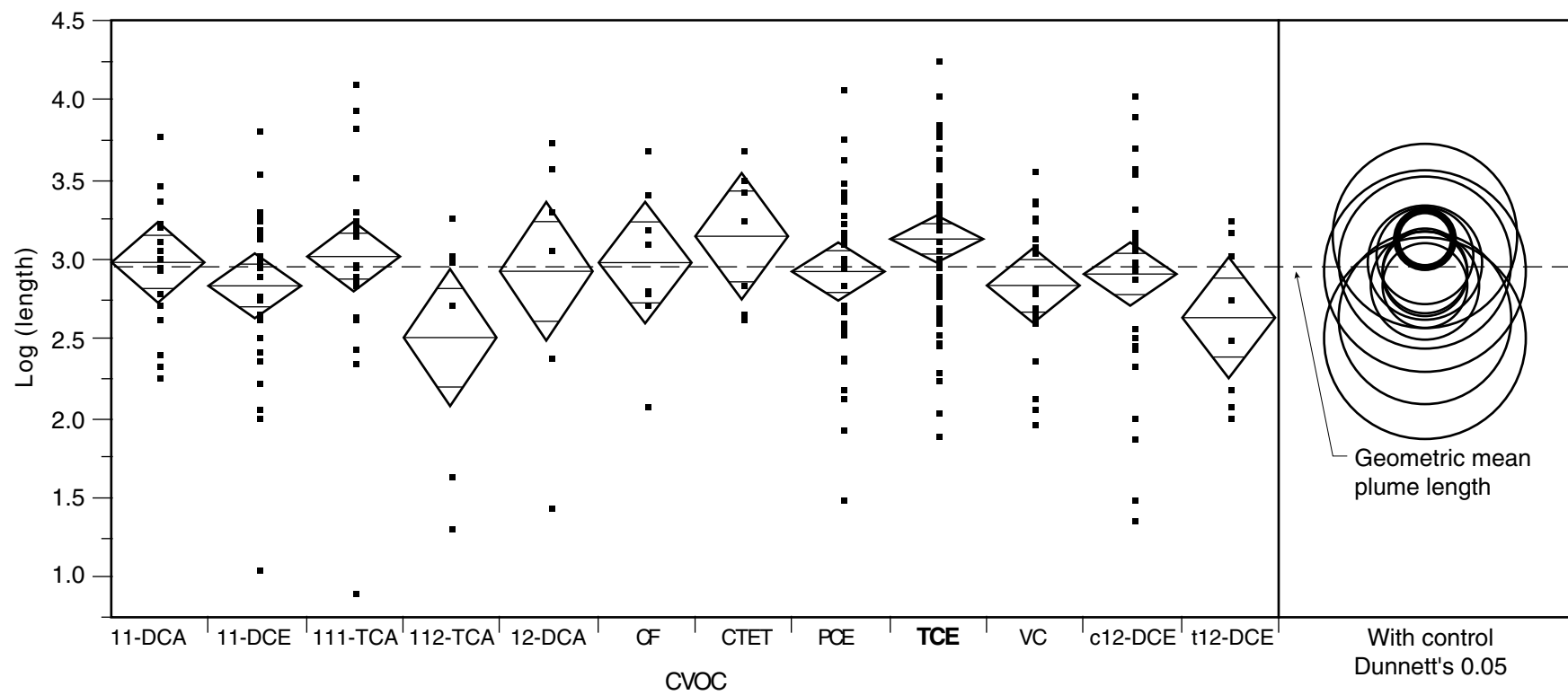
<b>Variables</b>	<b>Result</b>	<b>Result</b>
NONE	-1	0
STRONG	1	1
WEAK	0	-1
Estimate	-0.335	-0.363
Std Error	0.1149	0.1187
t Ratio	-2.92	-3.058
Prob>   t	0.0043	0.0029
SS	1.7249	1.8916

<b>Statistical parameters</b>	<b>Statistical results</b>
Sum of Squares	2.2501786762
Numerator DF	2
F Ratio	5.5604698798
Prob > F	0.0051174022

**Table C-5. Plume length means, least squares means and statistics from an analysis of covariance (ANCOVA) - log and original scale (ft).**

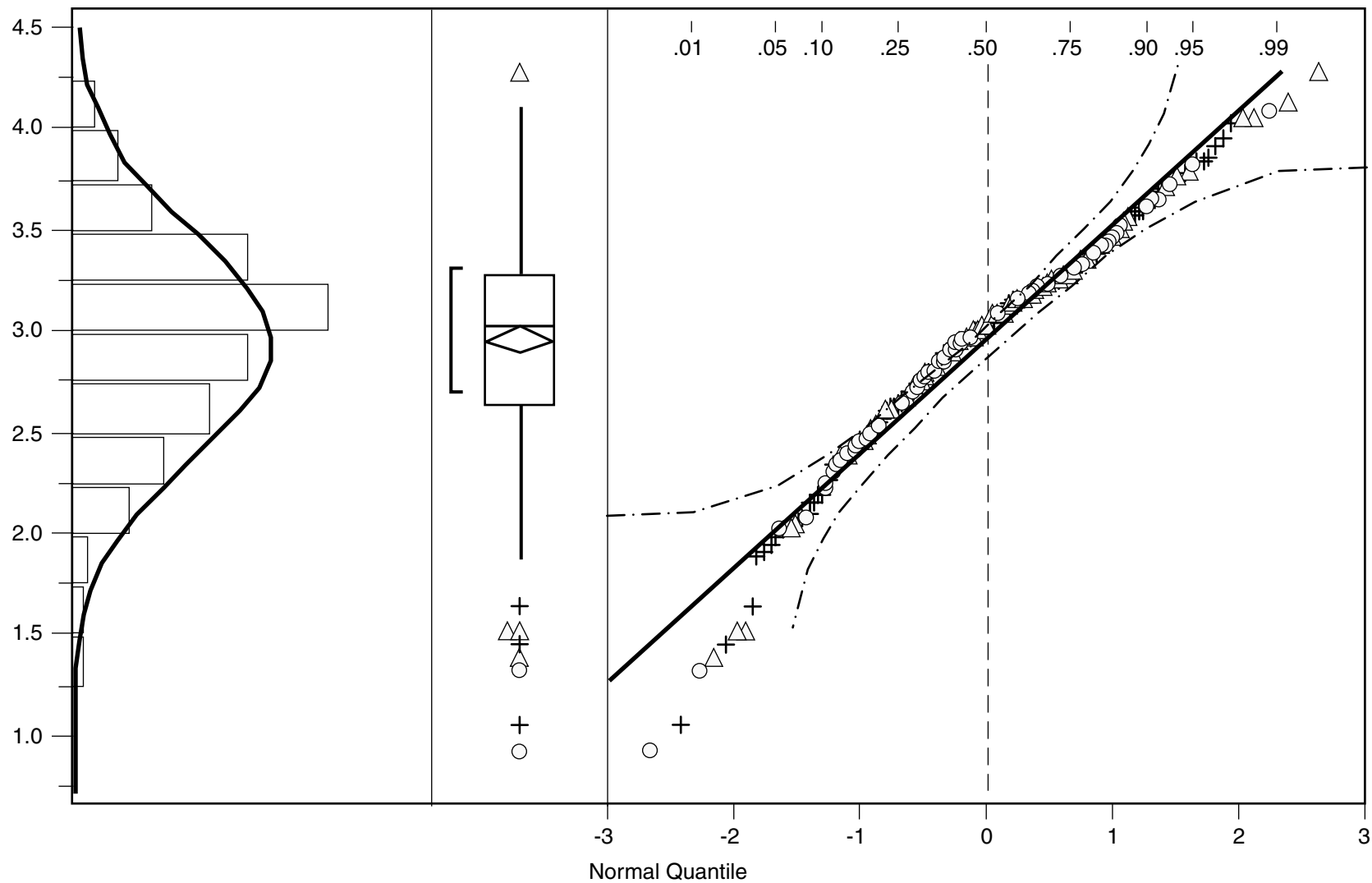
<b>Evidence<sup>a</sup></b>	<b>Sample size<sup>b</sup></b>	<b>Mean<sup>c</sup></b>	<b>Least squares mean<sup>c</sup></b>	<b>Standard error<sup>c</sup></b>	<b>Geometric mean<sup>d</sup> (original scale)</b>
<b><i>Data: All CVOC plumes</i></b>					
<b>Strong</b>	<b>37</b>	<b>2.759</b>	<b>2.703</b>	<b>0.078</b>	<b>508.2</b>
<b>Weak</b>	<b>51</b>	<b>3.006</b>	<b>3.023</b>	<b>0.066</b>	<b>1,059.7</b>
<b>None</b>	<b>41</b>	<b>2.989</b>	<b>3.019</b>	<b>0.073</b>	<b>1,051.2</b>
<b><i>Data: Without CVOC Daughter Plumes</i></b>					
<b>Strong</b>	<b>26</b>	<b>2.727</b>	<b>2.681</b>	<b>0.090</b>	<b>484.2</b>
<b>Weak</b>	<b>39</b>	<b>3.042</b>	<b>3.044</b>	<b>0.074</b>	<b>1,113.6</b>
<b>None</b>	<b>41</b>	<b>2.989</b>	<b>3.016</b>	<b>0.071</b>	<b>1,043.6</b>

<sup>a</sup> Evidence of reductive dehalogenation.<sup>b</sup> Number of plumes in each category of Evidence.<sup>c</sup> Rounded to three decimal places.<sup>d</sup> The bias corrected (Gilbert 1987) geometric mean is a sample estimate of the median (i.e., 50<sup>th</sup> percentile) on the original scale.



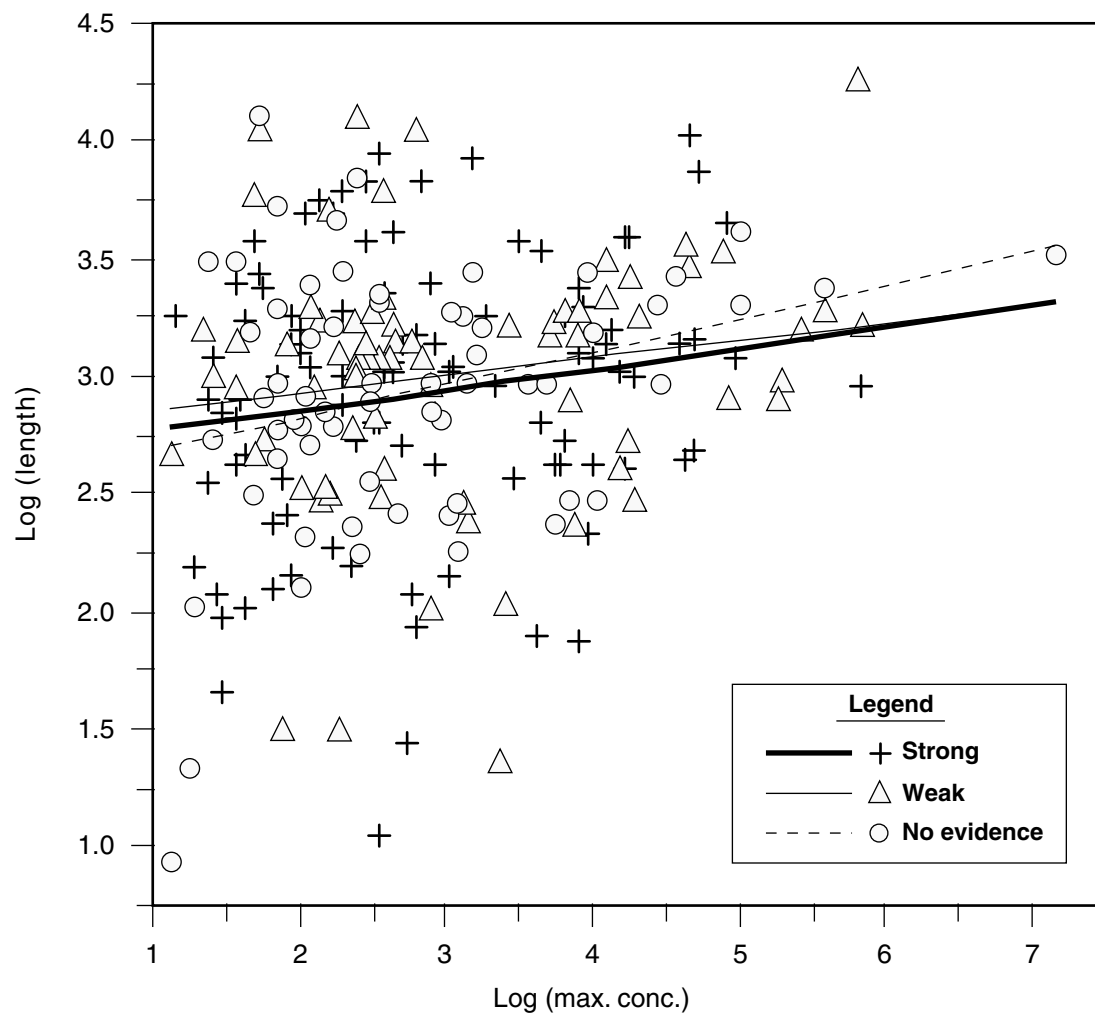
ERD-LSR-99-0043

Figure C-1. Plot of CVOC means and ANOVA test results.



ERD-LSR-99-0046

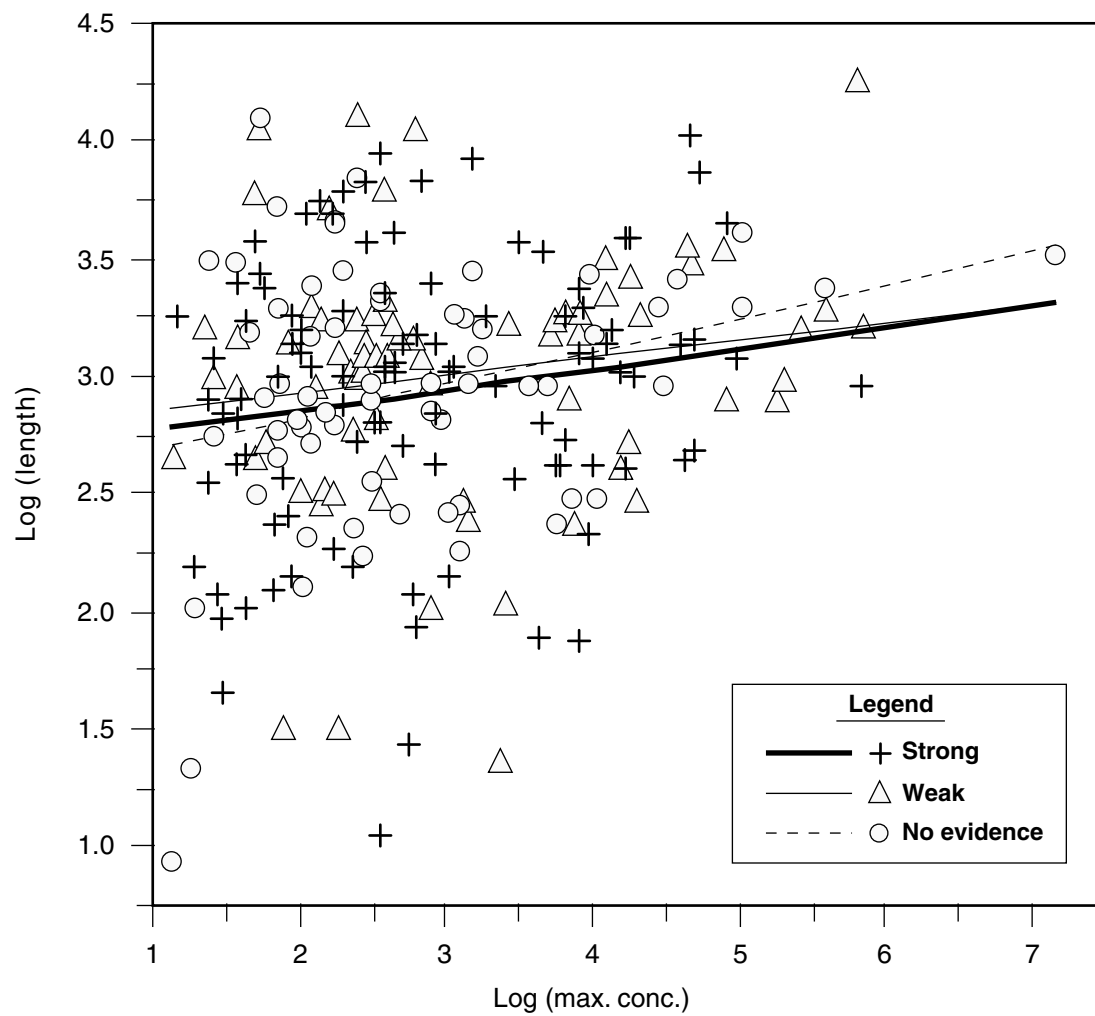
Figure C-2. Normality assumption test statistics for the common logs of plume length by histogram, box-and-whisker plot, normal quantile plot, and inference test results.



ERD-LSR-99-0047

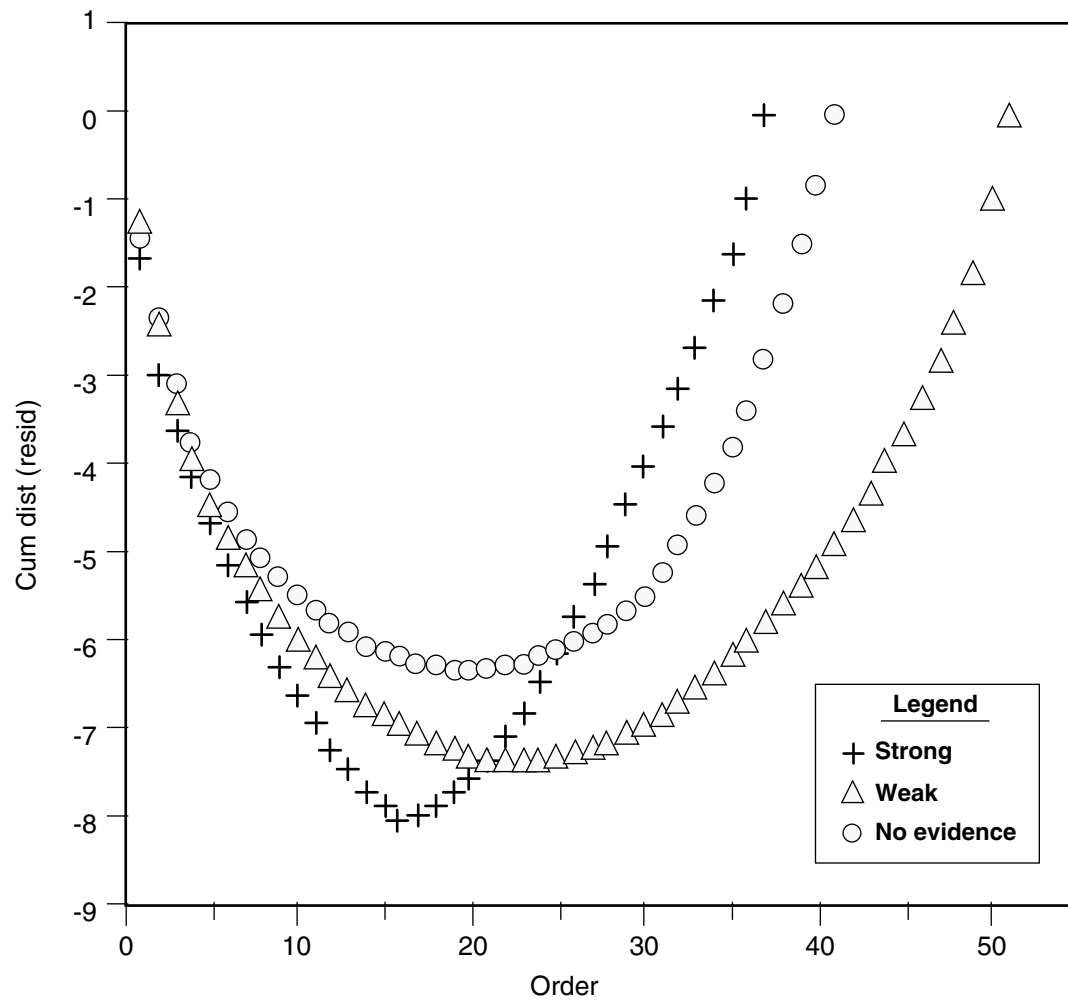
Figure C-3. Plot of Log (length) vs Log (max. conc.) for each category of evidence for reductive halogenation.





ERD-LSR-99-0048

Figure C-4. Plot of Log (length) vs Log (meanV) for each category of evidence for reductive dehalogenation.



ERD-LSR-99-0049

Figure C-5. Cumulative distributions of residuals from the ANCOVA model. The small minimum value for the strong reductive dehalogenation set is indicative of shorter-than-expected plume lengths after taking source concentration and groundwater velocity covariates into account. See text for explanation.

## **Appendix D**

### **CVOC Historical Case Analysis Plume Screening Checklist**

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## **Appendix D**

### **CVOC Historical Case Analysis Plume Screening Checklist**

The purpose of this Initiative is to evaluate the extent and behavior of chlorinated volatile organic compound (CVOC) groundwater plumes and, depending on the outcome of the data analysis, provide project managers with information to aid in decision making. Our working hypothesis is that the attributes of chlorinated solvent plumes, such as plume dimensions (length, width, thickness) and plume growth, have natural groupings. By identifying these natural groupings and data necessary for site evaluation, this document should help project managers to collect the appropriate data. This in turn should be an aid to the CVOC cleanup decision making process.

During 1997 the Initiative Data Collection Team will be collecting data on CVOC plume behavior. This screening checklist is intended to identify plumes that will be "nominated" for more in-depth data gathering. Plumes that qualify for the study must have sufficient data on fundamental factors such as advection, dispersion, sorption, and degradation.

This CVOC Plume Screening Checklist is intended to guide a case reviewer in determining if sufficient data is available to include a plume in the historical case analysis. The Plume Screening Checklist identifies key data requirements that must be available for a plume to be nominated for further evaluation. Nominated plumes will be reviewed by the Initiative Data Collection Team, who will complete a more extensive data collection checklist, and gather the data that will be entered into the historical case analysis database.

#### **D-1. Site Location, Points of Contact, and Reviewer**

This information is needed to identify the location of the plume and participant organization points of contact who performed the screening. In addition, the information is needed to identify points of contact for the responsible party and site consultant to facilitate electronic data gathering.

#### **D-2. Key Screening Questions**

These questions are placed early in the check list, so a person reviewing a given plume will not waste time on plumes that are not useful. If the answers are "yes" to these key questions, then it will be worthwhile to continue with the checklist.

#### **D-3. Explanation of Checklist Sections**

The CVOC Plume Screening Checklist is divided into ten sections. Each section is intended to provide important information need to perform the plume data collection process.

##### **1. Site Description and History**

Sites that have inadequate or no written site description or release history are excluded.

## 2. Chemicals of Concern

The major CVOCs of concern in the United States that impact groundwater are carbon tetrachloride (CT), tetrachloroethene (PCE), trichloroethene (TCE), 1,1,1-trichloroethane (TCA), 1,1,2-tetrachloroethane, and their CVOC daughter products chloroform (CF), methylene chloride (MC), cis- and trans-1,2-dichloroethene (cis-DCE, trans-DCE), 1,1-dichloroethene (1,1-DCE), vinyl chloride (VC), 1,1-dichloroethane (DCA), chloromethane, 1,2-dichloroethane (1,2-DCA), dichloromethane, and chloroethane (CA). Sites which do not have these CVOC compound as the primary contaminant are eliminated.

## 3. Extent and Duration of Groundwater Monitoring

Ideally, this study would only use data from sites where no plume remediation activities have been implemented. This is because remediation activities have great impacts in altering plume behavior, which of course is their purpose. However, excluding these sites would severely limit the number of sites eligible for the study. On the other hand, there are many sites that do have several years of groundwater monitoring data prior to implementation of groundwater remediation activities. This study will draw sites from both of these categories using the following screening criteria:

- *Concentrations of one or more CVOCs of interest (e.g., PCE, TCE) have exceeded 10 ppb in a number of plume wells.*
- *A meaningful plume length (distance from source area to downgradient leading edge) may be defined.*
- *Data are available prior to active remediation measures. This refers to any engineered attempt to influence the contaminant plume in the aquifer (exclusive of source area remediation).*
- *The primary contaminant plume does not daylight into surface water bodies before the 10 ppb contour.*
- *The CVOC groundwater monitoring analytical data are available in electronic form.*
- *There are measurements of hydraulic conductivity, and of the (x,y) coordinates of the groundwater monitoring wells at the site.*

## 4. Site Hydrogeology

Advection is one of the key processes that influence plume behavior. Sites which have not measured either groundwater flow velocity directly or taken measurements of hydraulic gradient, and hydraulic conductivity such that a groundwater flow velocity can be estimated, are eliminated. The hydrostratigraphy of a site is also an important influence on plume behavior. Sites where boring logs and/or cross sections are not available are also eliminated. Optional information includes lithology and organic carbon classification of the site. This information will be used to ensure that a variety of lithologies and organic carbon conditions are represented.

5. **Identification and Magnitude of Source and Release(s)**

The location and characterization of the source are important for understanding how plumes behave. Sites where the approximate location of the source has not been identified are eliminated. Optional information regarding the nature of the source is requested so that the Initiative Data Collection Team can select sites that represent a variety of source conditions.

6. **Groundwater Chemistry and Contaminant Fate**

Groundwater analytical data on general minerals, biodegradation geochemical indicator compounds, and potential carbon sources are key to understanding natural attenuation processes that are dominant within a given hydrogeologic setting. However, these data have only been collected at a minority of sites. The Initiative Data Collection Team will be interested in sites where this data has been collected and/or studied.

7. **Plume Dimensions and Behavior**

This optional information regarding plume dimensions and behavior is requested so that the Initiative Data Collection Team can select plume sites that represent a variety of sizes. This study will attempt to draw sites representing the wide range of plume sizes that occur in the United States. For example CVOC plume lengths can vary over four-orders-of-magnitude, from 10's to 10,000's of feet in length.

8. **Remediation Activities**

This optional information regarding remediation activities is requested so that the Initiative Data Collection Team can select sites with the longest period of pre-groundwater remediation monitoring. In addition, many CVOC plumes have had primary source removal either by actual physical removal of a leaking tank, excavation of a disposal area, or by hydraulic control of the secondary source area, without necessarily exercising hydraulic control on the distal portion of the plume. These sites will not be excluded from the study.

9. **General Comments on Suitability of Site for Inclusion in Study**

This is a general question that allows personal comments that might not be obvious to the Initiative Data Collection Team. Since the person filling out the plume screening checklist is expected to be an individual with a good understanding of the site, they may have comments, opinions, or anecdotal information that could be helpful in the nomination and screening process.

10. **Data Requested in Electronic or paper Form**

This is a listing of the data that is being requested. It is preferred that as much of the data as possible be in electronic form. The most important data are the CVOC groundwater monitoring well analytical chemistry data, and the (x,y) coordinates for the monitoring wells. These data must be in electronic form. All other data are acceptable in electronic form.

## Chlorinated VOC Plume Screening Checklist

### Site Location, Points of Contact, and Reviewer

Site name: \_\_\_\_\_  
Alternate site names (aliases): \_\_\_\_\_  
City: \_\_\_\_\_  
State: \_\_\_\_\_  
Zip code: \_\_\_\_\_

Agency project manager: \_\_\_\_\_  
Agency name \_\_\_\_\_  
Street Address: \_\_\_\_\_  
City: \_\_\_\_\_  
State: \_\_\_\_\_  
Zip code: \_\_\_\_\_  
Phone number: \_\_\_\_\_  
Email (if available) \_\_\_\_\_

Person filling out this form: \_\_\_\_\_  
(if other than project manager)  
Associated agency: \_\_\_\_\_  
Street Address: \_\_\_\_\_  
City: \_\_\_\_\_  
State: \_\_\_\_\_  
Zip code: \_\_\_\_\_  
Phone number: \_\_\_\_\_  
Email (if available) \_\_\_\_\_

Consultant name: \_\_\_\_\_  
Company name: \_\_\_\_\_  
Street Address: \_\_\_\_\_  
City: \_\_\_\_\_  
State: \_\_\_\_\_  
Zip code: \_\_\_\_\_  
Phone number: \_\_\_\_\_  
Email (if available) \_\_\_\_\_

Responsible Party Contact: \_\_\_\_\_  
Company: \_\_\_\_\_  
Street Address: \_\_\_\_\_  
City: \_\_\_\_\_  
State: \_\_\_\_\_  
Zip code: \_\_\_\_\_  
Phone number: \_\_\_\_\_  
Email (if available) \_\_\_\_\_

Date this form completed: \_\_\_\_\_



## Key Screening Questions

Are the most significant chemicals of concern in groundwater at this site any of the following CVOCs:

yes no

carbon tetrachloride (CT), tetrachloroethene (PCE), trichloroethene (TCE) , or 1,1,1-trichloroethane (TCA), or their daughter CVOC products [(i.e., chloroform (CF), methylene chloride (MC), cis- and trans-1,2-dichloroethene (*cis*-DCE, *t*-DCE), 1,1-dichloroethene (1,1-DCE), vinyl chloride (VC), 1,1-dichloroethane (DCA), or chloroethane (CA)]?

- Have the concentrations of one or more CVOCs of interest (e.g., PCE, TCE) exceeded 10 ppb in a number of plume wells? yes no
- Can a meaningful plume length (distance from source area to downgradient leading edge) be defined? yes no
- Are data available prior to active remediation measures.? This refers to any engineered attempt to influence the contaminant plume in the aquifer (exclusive of source area remediation). yes no
- Is the CVOC groundwater monitoring analytical data available in electronic form? yes no
- Are the (x,y) coordinates of the groundwater monitoring wells known? yes no

*IF THE ANSWER TO ANY OF THE ABOVE QUESTIONS IS NO, DO NOT FILL OUT THE REMAINDER OF THIS FORM.*

## Electronic Data

The CVOC groundwater monitoring analytical data in electronic form is a minimum requirement. Please see page A-10 for a listing of requested paper and electronic data. The electronic data may be provided in any format that is convenient. The preferred formats are MS ACCESS tables or databases, Excel spreadsheets, tab-delimited text files, or MS Word documents, and any electronic version of site maps in AutoCAD (.DWG or .DXF) or ArcView/ArcINFO (.shp or .e00) formats. The data can be mailed on 3.5 inch PC-compatible disks, ZIP disks, or sent via internet by individual arrangement. Internet transmission is preferred.

Please list the content and format of the electronic data available for this site:

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## 1. Site History

### 1.1 Is a site description and contaminant release history available?

yes      no

## 2. Chemicals of Concern

**2.1. Insert an (X) in the following table to identify the chlorinated hydrocarbons that are *significant* constituent(s) of concern (COCs) and which are present in the groundwater.**

Check (X)	Chemical
	Carbon tetrachloride
	Chloroethane
	Chloroform
	Chloromethane
	Dichloroethane, 1,1-
	Dichloroethane, 1,2-
	Dichloroethylene, 1,1-
	Dichloroethylene, cis-1,2-
	Dichloroethylene, trans-1,2-
	Dichloromethane
	Methylene chloride*
	Tetrachloroethane, 1,1,2,2-
	Tetrachloroethylene
	Trichloroethane, 1,1,1-
	Trichloroethylene
	Vinyl chloride

\*Possible lab contaminant.

### 2.2. List of any other chemicals found at significant levels in groundwater:

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### 3. Extent and Duration of Groundwater Monitoring

#### 3.1. Number of monitoring wells associated with the plume

- a. within the affected water-bearing zone \_\_\_\_\_
- b. within overlying/underlying units \_\_\_\_\_

#### 3.2. Year monitoring began \_\_\_\_\_

#### 3.3. Have monitoring wells within the affected water-bearing zone(s) been generally sampled on a regular routine schedule? yes    no

#### 3.4. Total number of years monitoring wells have been sampled \_\_\_\_\_

#### 3.5. Has groundwater remediation commenced? yes    no

If yes:

Number of years monitoring wells were sampled prior to initiation of groundwater remediation: \_\_\_\_\_

Number of sampling events prior to initiation of groundwater remediation: \_\_\_\_\_

Number of years monitoring wells were sampled after groundwater remediation was discontinued: \_\_\_\_\_

Number of sampling events after groundwater remediation was discontinued: \_\_\_\_\_

#### 3.6. Has the plume been monitored or sampled with depth-discrete sampling methods? yes    no

### 4. Site Hydrogeology

#### 4.1. Are there multiple geologic units? yes    no

4.1.1. Provide a brief description of the site geology \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

**4.2. Are there measurements of:**

hydraulic gradient?	yes	no
porosity?	yes	no
hydraulic conductivity in the plume?	yes	no

**4.3. Are there boring logs available?**

<b>yes</b>	<b>no</b>
------------	-----------

Are depth of hydrostratigraphic contacts at boring location available?

yes	no
-----	----

**4.4 Have the well elevations and locations been surveyed?**      yes      no

**5. Identification and Magnitude of Source and Release(s)**

**5.1. Have the source location(s) been approximately identified**      yes      no

**5.2. Are there multiple CVOC source areas?**      yes      no

5.2.1. If yes, do the primary CVOC plumes co-mingle?      yes      no

5.2.2. If yes, can their lengths be defined at the 10 ppb contour?      yes      no

**6. Groundwater Chemistry and Contaminant Fate:****6.1 Which of the following plume general minerals, biodegradation geochemical indicators compounds, and potential carbon sources were measured? (circle)**

Alkalinity	Iron, dissolved or Fe(II)
Ammonia	Manganese
Carbon dioxide (CO <sub>2</sub> )	Methane
Chloride	Nitrate/nitrite
Dissolved organic carbon	pH
Dissolved oxygen (O <sub>2</sub> )	Phosphate
Ethane	Redox potential (Eh or pE)
Ethene (ethylene)	Specific Conductivity (EC)
Fatty acids	Sulfate
Hydrogen (H <sub>2</sub> )	Sulfide
Other _____	Temperature

**6.2. Were any natural attenuation or biodegradation studies performed at the site?**

yes	no
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If yes, describe:

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## 7. Plume Dimensions and Behavior:

### 7.1. Has the CVOC groundwater contaminant plume been contoured?

yes no

### 7.2. Are there any indications of any special conditions that are affecting plume behavior, (e.g., structures such as sewer and water lines, or sumps)?

yes no

If yes, describe

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### 7.3. Is the primary CVOC plume daylighting into a river or lake, and truncating after the 10 ppb contour?

yes no

If yes, describe

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### 7.4. Are there pumping wells, which distort the plume, and interfere with natural plume behavior?

yes no

If yes, describe

---

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---

## 8. Remediation Activities

### 8.1 Have soil, groundwater, or vapor removal activities been performed in source area?

yes no

If yes, describe

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### 8.2 Have plume groundwater remediation activities been performed?

yes no

If yes, approximate date remediation began \_\_\_\_\_

If yes, approximate date remediation was discontinued \_\_\_\_\_

### 8.3 Short description of remediation activities (i.e., cycling, multiple methods, etc.)

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## 9. General Comments on Suitability of Site for Inclusion in Study

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## 10. Check if Available in Paper or Electronic Form {*electronic is preferred*}

### 10.1. Site Investigation Data

Paper	Elec.	
<input type="checkbox"/>	<input checked="" type="checkbox"/>	Groundwater sample analytical data from each well through time (including CVOCs, minerals, etc.) { <i>electronic is required</i> }
<input type="checkbox"/>	<input type="checkbox"/>	Groundwater elevation & depth to groundwater measurements through time
<input type="checkbox"/>	<input type="checkbox"/>	Soil analytical data from borings or other samples
<input type="checkbox"/>	<input type="checkbox"/>	DNAPL/LNAPL analytical data
<input type="checkbox"/>	<input type="checkbox"/>	Soil & groundwater test data (porosity, bulk density, moisture, toc, etc.)
<input type="checkbox"/>	<input type="checkbox"/>	Aquifer pumping test results (i.e., transmissivity, conductivity)
<input type="checkbox"/>	<input type="checkbox"/>	Boring logs, x, y coordinates for wells, geologic description logs, depths of hydrostratigraphic contacts
<input type="checkbox"/>	<input type="checkbox"/>	Well construction logs (screen depths) (summary tables, if available)

### 10.2. Maps and Cross Sections

Paper	Elec.	
<input type="checkbox"/>	<input type="checkbox"/>	Regional site location map
<input type="checkbox"/>	<input type="checkbox"/>	Site maps showing physical features (topography, roads, sewerlines, drains)
<input type="checkbox"/>	<input type="checkbox"/>	Site maps showing monitoring well locations, and boring locations
<input type="checkbox"/>	<input type="checkbox"/>	Site maps showing source locations
<input type="checkbox"/>	<input type="checkbox"/>	Site maps showing groundwater elevation contours
<input type="checkbox"/>	<input type="checkbox"/>	Map of nearby wells and surface water bodies
<input type="checkbox"/>	<input type="checkbox"/>	Isocontour maps of COCs in groundwater
<input type="checkbox"/>	<input type="checkbox"/>	Isocontour maps of COCs in soil
<input type="checkbox"/>	<input type="checkbox"/>	Site maps showing locations of SVE wells & groundwater extraction wells
<input type="checkbox"/>	<input type="checkbox"/>	Geologic maps and cross-sections along and normal to axis of plume core

### 10.3 Narratives

- \_\_\_\_\_ Site Description
- \_\_\_\_\_ Site Geology
- \_\_\_\_\_ Release History
- \_\_\_\_\_ Site Investigations (summary, if available)
- \_\_\_\_\_ Remediation History

**\*Hard Copy Data:**

*Typically, an RI/FS will provide this information on site history, site description, and site characterization documents.*





## **Appendix E**

### **Statistical Analysis of VOCs in the Environment (SAVE) Relational Data Base Elements**

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**Table E-1. SAVE Database element fields: Measured, Derived, and Interpreted**

<i>Table</i>	<i>Related Table</i>	<i>Parameter</i>	<i>Description</i>	<i>Domain</i>	<i>Format</i>	<i>Origin</i>
<b>SiteInfo</b>		SEQNO	Sequence number		nnnnnnnnn	Assigned
		SITENAME	Site name		text	Measured
		STREETNO	Street number			Measured
		STREET	Street name		text	Measured
		XSTREET	Cross street		text	Measured
		CITY	City		text	Measured
		COUNTY_LIST	County	CA/OR counties 1-99	nn	Measured
		STATE_LIST	State		nn	Measured
		State_List	State Census # 1-99			
		ZIP	Zip code			Measured
		LAT	Latitude			Measured
		LON	Longitude			Measured
		DNAPL	Are DNAPLS present (y/n)		y/n	Measured
		LNAPL	Are LNAPLS present (y/n)		y/n	Measured
		AV_PRECIP(INCHES/YEAR)	Average precipitation		nnnn.nn	Measured
		AV_WIND_SPEED(MPH)	Average wind speed		nnnn.nn	Measured
		AV_TEMP(DEGREES_F)	Average temperature		nnn.nn	Measured
		AV_HUMIDITY(%)	Average humidity		nn.nn	Measured
		AV_EVAPOTRNS(INCHES/YR)	Average evapotranspiration		nnnn.nn	Measured
		DISCOVERY_DATE	Contamination discovery date		m/d/y	Measured
		GEOLOGIC_SETTING_LIST	Geologic region 1-15		nn	Measured
		Geo_Setting_List	Freeze and Cherry's USGS Geologic Regions			
<b>BoreInfo</b>		SEQNO	Sequence number		nnnnnnnnn	Assigned
		BORENAME	Bore name		text	Records
		BOREDATE	Completion date		m/d/y	Measured
		X(EASTING)	Easting (feet) state plane or local coords.		nnnnnnnn.nn	Measured
		Y(NORTHING)	Northing(feet) state plane or local coords.		nnnnnnnn.nn	Measured
		POINT_OF_MEASUREMENT	Datum (e.g. surface, casing top)		text	Observed
		ELEVATION_AT_POM(FEET)	Elevation		nnnn.nn	Measured
		DEPTH(FEET)	Depth lowest point in well		nnnnnn.nn	Measured
		DEPTH_1ST_WATER(FEET)	Depth of first water		nnnn.nn	Measured
		BORE_TYPE_LIST	Bore type classification		letter	A-H
	Bore_Type_List		Bore type letters			
		IN_PLUME?	Is the well screened in the plume?		y/n	

**Table E-1. SAVE Database element fields: Measured, Derived, and Interpreted**

<i>Table</i>	<i>Related Table</i>	<i>Parameter</i>	<i>Description</i>	<i>Domain</i>	<i>Format</i>	<i>Origin</i>
<b>ChemSample</b>		SEQNO	Sequence number		nnnnnnnnnn	Assigned
		BORENAME	Bore name		text	Measured
		DATE	Date		m/d/y	Measured
		MATRIX	Matrix (e.g. SOIL, WATER, VAPOR)		text	Measured
		CHEM_NUMBER	Chemical number		nnnnnnnnnn	See List
		ANALYTE_NAME	(e.g. TPH, TotalVOCs,eH,pH)		text	Measured
		QUALIFIER	Letter/symbol for accuracy		text	Measured
		CONCENTRATION	Concentration		text/nnnnn.n	Measured
		DETECTION_LIMIT	Detection limit		nnnn.nn	Measured
		DILUTION_FACTOR	Dilution factor		nnnn.nn	Measured
		UNITS	Units		text	Measured
		ANALYTICAL_METHOD	Analytical method		text	Measured
	Chem_List	CHEMICAL	Analyte name		text	Assigned
		CHEM_NUMBER	Chemical number		nnnnnnnnnn	Assigned
		CAS_NUMBER	CAS number		nnnnnnnnnn	Assigned
		ALIAS	Abbreviation of chem name		text	Assigned
<b>WaterLevel</b>		SEQNO	Sequence number		nnnnnnnnnn	Assigned
		BORENAME	Bore name		text	Measured
		DATE	Date		m/d/y	Measured
		DEPTH_TO_GW(FEET)	Ground water depth		nnnnn.nn	Measured
		POINT_OF_MEASUREMENT	Datum (e.g. surface, casing top)		text	Observed
		GW_ELEV.(FEET_AMSL)	Ground water elevation		nnnnn.nn	Measured
		VADOSE_ZONE_THICK(FEET)	Thickness of vadose zone at well			
<b>AquiferTest</b>		SEQNO	Sequence number		nnnnnnnnnn	Assigned
		SITE_AVG_K(FT/DAY)	Sitewide average hydraulic conductivity		nnnn.nn	Derived
		LO_K	Sitewide lowest K value reported		nnnn.nn	Derived
		HI_K	Sitewide highest K value reported		nnnn.nn	Derived
		GEOMEAN_K	Geometric mean of K values at site		nnnn.nn	Derived
		STDEV_K	Standard deviation of K values at site		nnnn.nn	Derived
		NUMBER_OF_K_VALUES	Number of K values measured		nnnn.nn	Derived
		GEOMEAN_TRANSMISSIVITY	Geometric mean of T values at site		nnnn.nn	Derived
		STDEV_T	Standard deviation of T values at site		nnnn.nn	Derived
		NUMBER_OF_T_VALUES	Number of T values measured		nnnn.nn	Derived
		COMMENTS	Converting units and other notes		nnnn.nn	Derived

**Table E-1. SAVE Database element fields: Measured, Derived, and Interpreted**

<i>Table</i>	<i>Related Table</i>	<i>Parameter</i>	<i>Description</i>	<i>Domain</i>	<i>Format</i>	<i>Origin</i>
<b>Plume_Remediation</b>		SEQNO	Sequence number		nnnnnnnnnn	Assigned
		PLUME_NUMBER	Plume number		nn	Assigned
		REMED_START_DATE	Remediation start date		m/d/y	Measured
		REMED_END_DATE	Remediation end date		m/d/y	Measured
		EST_MASS_REMOVED(G)	Estimated mass removed		nnnnnnnn.nn	Derived
		REMEDICATION_METHOD	Remediation method		letter	Measured
				A=Slurry wall/grout curtain		Measured
				B=In Situ bio-remediation		Measured
				C=Soil/rock excavation		Measured
				D=Tank removal		Measured
				E=Air sparging		Measured
				F=Ground water extraction		Measured
				G=Soil vapor extraction		Measured
<b>Hydro_Desc</b>		SEQNO	Sequence number		nnnnnnnnnn	Assigned
		EFFECTIVE_POROSITY(%)	Effective porosity (fraction)		nnnn.nnnnn	Interpreted
		AV_DEPTH_WATER_TABLE	Average depth to water table		nnnn.nnnnn	Interpreted
		HYDRO_GRADIENT	Hydraulic gradient		nnnn.nnnnn	Interpreted
		ORGANIC_CARBON_CONT.	Organic carbon content		nnnnn.nn	Interpreted
		RECHARGE_INFIL(FT/DAY)	Recharge infiltration		nnnnn.nn	Interpreted
		AV_AQUIFER_THICKNESS(FT)	Average Aquifer thickness		nnnnn.nn	Interpreted
<b>Plume_Dat</b>		SEQNO	Sequence number		nnnnnnnnnn	Interpreted
		PLUME_NUMBER	Plume number		nn	Assigned
		PLUME_CONTAMINANT	Plume contaminant alias name		text	Interpreted
		SOURCE_X(EASTING)	Source easting		nnnnnnnnn.nn	Interpreted
		SOURCE_Y(NORTHING)	Source northing		nnnnnnnnn.nn	Interpreted
		PLUME_DATE	Plume date		m/d/y	Interpreted
		PLUME_LENGTH(FEET)	Plume length		nnnn.nn	Interpreted
		PLUME_WIDTH(FEET)	Plume width		nnnn.nn	Interpreted
		IMPACTED_WTR_VOL(GAL)	Volume of impacted water		nnnnnnnnn.nn	Interpreted
		MAX_CONC(PPB)	Maximum concentration		nnnn.nn	Measured
		MAX_CONC_X(EASTING)	X Coordinate of max concentration		nnnnnnnnn.nn	Interpreted
		MAX_CONC_Y(NORTHING)	Y Coordinate of max concentration		nnnnnnnnn.nn	Interpreted
		AV_CONCENTRATION(PPB)	Average concentration		nnnn.nn	Derived
		RETARDATION_COEFF	Retardation coefficient		nnnn.nn	Derived
		PLUME_DAYLIGHT	Plume daylights (y/n)		y/n	Measured
		REMOVE_STAT_ANAL.	Yes or No flag for plume removal		y/n	Derived
		SUMP_IN_PLUME	Are sumps in use (y/n)		y/n	Measured
		SIG_IMPACT_FROM_SUMP	Do these sumps impact plume		y/n	Derived
		RELEASE_START_DATE	Release start date		m/d/y	Measured
		MATERIALS_RELEASED	List of chemicals spilled		text	Measured
		MASS/VOL_RELEASED	Quantity of spill		text	Measured
		UNITS	Units used to measure quantity		text	Measured
		RELEASE_END_DATE	Release end date		m/d/y	Measured

**Table E-1. SAVE Database element fields: Measured, Derived, and Interpreted**

<i>Table</i>	<i>Related Table</i>	<i>Parameter</i>	<i>Description</i>	<i>Domain</i>	<i>Format</i>	<i>Origin</i>
<b>Super_Plume</b>		SEQNO	Sequence number		nnnnnnnnnn	Assigned
		PLUME_NUMBER	Plume number		nn	Assigned
		GROWTH_RATE(FT3/YEAR)	Growth rate		nnnn.nn	Interpreted
		MEAN_GRAD_DIRECTION	Mean gradient direction		text	Interpreted
		MEAN_GRAD_MAGNITUDE	Mean gradient magnitude		nnnn.nn	Interpreted
		MEAN_GRAD_STD	Mean grad. standard deviation		nnnn.nn	Interpreted
		MEAN_VERT_GRAD_MAG	Mean vertical grad. magnitude		nnnn.nn	Interpreted
		MAX_GRAD_DIRECTION	Maximum gradient direction		text	Measured
		MAX_GRAD_MAGNITUDE	Maximum gradient magnitude		nnnn.nn	Measured
		MAX_GRAD_STD	Max grad. standard deviation		nnnn.nn	Measured
		MIN_GRAD_DIRECTION	Minimum gradient direction		text	Measured
		MIN_GRAD_MAGNITUDE	Minimum gradient magnitude		nnnn.nn	Measured
		MIN_GRAD_STD	Min grad. standard deviation		nnnn.nn	Measured
		MEAN_VELOCITY	Mean velocity		nnnn.nn	Interpreted
		MAX_VELOCITY	Maximum velocity		nnnn.nn	Measured
		MIN_VELOCITY	Minimum velocity		nnnn.nn	Measured
		MASS_CHANGE(G/YEAR)	Mass change		nnnn.nn	Interpreted
		INTERP_DEG_RATE	Interpreted degradation rate		nnnn.nn	Interpreted
		DEGRATE_MTHD_LIST	Interp. deg. rate method		letter	Interpreted
			A=Interp. deg. rate method			Interpreted
			B=Lab microcosm study			Interpreted
			C=Literature review			Interpreted
			D=Transportation model calibr.			Interpreted
			E=Buscheck/Alcantar plume int.			Interpreted
			F=Recalcitrant tracer analyses			Interpreted
			G=Parent/daughter prod. ratio anal.			Interpreted
			H=Chloride mass balance			Interpreted

## **Appendix F**

### **Summary of CVOC Historical Case Analysis Site Hydrogeologic Conditions**

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<b>Table F-1. Summary of CVOC Historical Case Analysis Initiative site hydrogeologic conditions.</b>					
<b>Sequence Number</b>	1200	6240001	6240002	5301	5302
<b>Facility Type</b>	DOD	DOD	DOD	DOD	DOD
Start/Stop Operations	1965 - 1985	1941 - PRESENT	1941 - PRESENT	1951-1967	
Release dates					
Discov. Date					
Est. mass/vol of release					
DNAPL detected?				NO	
Year monitoring began	1987	1980	1987		1988 OR 1995
Remed. start	NONE	1994	1997		Mar-96
# yrs. pre-remed. data	11	14	10		
# of monitoring wells		250	21		150+
Semi-con. sediments					
Unconsolidated sediments				X	
Fractured porous rock					
Fractured non-porous rock					
Depth to gw (FT. BGS)					
Organic carbon	0.017 - 0.0836				
Kd or Koc					
Zone confined /unconfined	UNCONFINED	SEMI-CONFINED			UNCONFINED
Sitewide K (FT/DAY)	41.76			0.05	
Low K	24.48	12	12	0.006	16
Hi K	70.56	300	300	80	602
Geomean K		67.48095902	67.48095902	0.029136935	98.03253008
Stdev K		132.3177993	132.3177993		121.1547944
# K values		4	4		
Horiz. grad.(FT/FT)	0.0008	0.16	0.16	0.000756547	
GW velocity(FT/DAY)	0.031				
GW flow direction	SW/W	SW	SW		
Source removed?	NO	YES	YES		NO
Method of removal		SVE	SVE		
Date of removal		1994	1998		
Type of Pump&Treat		CONTINUOUS OP			
Start date		5/1/94			
Stop date		10/1/97			
Other remediation	PILOT BIOVENT				EXTR. WELLS
Start date	1993				Sep-96
Stop date					?
In-situ biorem.?					

<b>Seqno</b>	4901	6380002	6380005	4700	6430008
<b>Facility Type</b>	DOD	DOD	DOD	DOD	DOD
Start/Stop Operations			1960 - PRESENT	1942 - 1990	1933 - PRESENT
Release dates	1967-1975			1942 - 1982	? - 1980
Discov. Date					
Est. mass/vol of release	110,000GALS DNAPL				
DNAPL detected?	YES			NO	
Year monitoring began	1986		1991	1995	1987
Remed. start			NONE	NONE	NONE
# yrs. pre-remed. data	3		4	3	11
# of monitoring wells	50		4	31	144
Semi-con. sediments					
Unconsolidated sediments				X	X
Fractured porous rock					
Fractured non-porous rock					
Depth to gw (FT. BGS)	20-Oct	5.5 - 8		15-May	Oct-55
Organic carbon				0.001	
Kd or Koc					
Zone confined /unconfined				UNCONF TO SEMI-CONF	UNCONF TO SEMI-CONF
Sitewide K (FT/DAY)			0.66	5.3	
Low K		0.0018	0.011		2.6
Hi K		560	6.55		90.7
Geomean K		0.393739986	0.132374651		15.175483
Stdev K		196.0156236	1.849833971		49.68172031
# K values		8	12		4
Horiz. grad.(FT/FT)		0.001	0.003	0.003	0.0045
GW velocity(FT/DAY)				0.05753	
GW flow direction		SW	N/NE	N	N
Source removed?	YES		NO	NO	NO
Method of removal	EXT WELLS/SVE				
Date of removal	1986-PRESENT				
Type of Pump&Treat			NONE	NONE	
Start date	1986?				
Stop date	?				
Other remediation					
Start date					
Stop date					
In-situ biorem.?				YES	

Seqno	6430009	340001	6560001	6390001	6480002
Facility Type	DOD	DOD	DOD	DOD	DOD
Start/Stop Operations	1933 - PRESENT		1945 - PRESENT	1972 - 1983	
Release dates	? - 1980		LATE 1950S - 1989		1967-1978
Discov. Date					
Est. mass/vol of release					
DNAPL detected?					
Year monitoring began	1987		1994	1988	1997
Remed. start	NONE				NONE
# yrs. pre-remed. data	11		4	8	
# of monitoring wells	144	28	78	8	4
Semi-con. sediments					
Unconsolidated sediments	X		X	X	
Fractured porous rock					
Fractured non-porous rock					
Depth to gw (FT. BGS)	5		5	3.3-9.3	23
Organic carbon					
Kd or Koc					
Zone confined /unconfined	UNCONF TO SEMI-CONF	UNCONFINED			
Sitewide K (FT/DAY)			28.3	0.06	6.7
Low K	2.6	1.09			4
Hi K	90.7	5.44			9.4
Geomean K	15.175483	2.28423344			
Stdev K	49.68172031	2.292516812			
# K values	4	3			
Horiz. grad.(FT/FT)	0.0045	0.0044	0.0055	0.008	
GW velocity(FT/DAY)					0.2
GW flow direction	N	SW	SOUTH	S	
Source removed?	NO		YES		YES
Method of removal			TANK AND SOIL REVOVAL	SOIL EXTRACTION	NEUT. PIT REMOVED
Date of removal				1994	7/93?
Type of Pump&Treat			NONE		
Start date					
Stop date					
Other remediation					
Start date					
Stop date					
In-situ biorem.?			NO		

<b>Seqno</b>	6380004	5303	2901	802	3905
<b>Facility Type</b>	DOD	DOE	DOE	DOE	DOE
Start/Stop Operations	1946 - 1995	1936 -1987	NO REPORT OR CHECKLIST		1952-?
Release dates		1955-1973		1954-1958	1952-1986
Discov. Date				1997	
Est. mass/vol of release		577,000-922,000KG CTET		UNK	20,000-200,000gal of TCE
DNAPL detected?				NO	YES
Year monitoring began	1994	1986		1990	1986
Remed. start					
# yrs. pre-remed. data				7	9
# of monitoring wells	8	150		22	55
Semi-con. sediments					
Unconsolidated sediments	X				
Fractured porous rock					
Fractured non-porous rock					
Depth to gw (FT. BGS)	5.9-6.7			13-Jan	
Organic carbon					
Kd or Koc					
Zone confined /unconfined	UNCONFINED	UNCONFINED			
Sitewide K (FT/DAY)					
Low K		9.905		0.2547	339.6
Hi K		56.6		1.698	1924.4
Geomean K		23.68		0.6576	465.0686
Stdev K		33.02		1.02	713.2678
# K values		2			5
Horiz. grad.(FT/FT)	0.0001				
GW velocity(FT/DAY)					
GW flow direction	SE	W		N	
Source removed?		YES		YES	
Method of removal		SVE		DRUM/SOIL REMOVAL	
Date of removal		1995		1970/1997	
Type of Pump&Treat					EXTRACTION WELLS
Start date					Aug-95
Stop date					ONGOING
Other remediation					
Start date					
Stop date					
In-situ biorem.?					

Seqno	3901	3904	3903	6010002	6010003
Facility Type	DOE	DOE	DOE	DOE	DOE
Start/Stop Operations	1954 - 1988				
Release dates			1953 - 1989	1960 - 1980's	1962 - 1978
Discov. Date					1982
Est. mass/vol of release					500 gal
DNAPL detected?	YES			NO	YES
Year monitoring began	1988	1987	1988	1982	1990
Remed. start	1991	1991	1950's	NONE	?
# yrs. pre-remed. data	3	4	0	16	8
# of monitoring wells	84	11			
Semi-con. sediments		X			
Unconsolidated sediments		X			
Fractured porous rock				X	X
Fractured non-porous rock					
Depth to gw (FT. BGS)				0 - 70	
Organic carbon					
Kd or Koc					
Zone confined /unconfined				UNCONFINED	
Sitewide K (FT/DAY)			37		
Low K	0.8	4			0.005094
Hi K	1.6	6			12.169
Geomean K	1.1131	4.898979486		1.346114968	0.707502088
Stdev K	0.5656	1.414213562		1.357430248	3.00490186
# K values	2	2		10	20
Horiz. grad.(FT/FT)		0.01	0.015	0.035355339	0.1
GW velocity(FT/DAY)	0.000821				
GW flow direction		N/S DIVIDE E/W FLOWS		S/SE	S/SW
Source removed?	YES		YES	NO	YES
Method of removal	SOIL REMOVAL		PUMPING IN SOURCE AREA		SOIL REMOVAL
Date of removal	?				
Type of Pump&Treat	EXTRACTION WELLS	TRENCHES & EXTR. WELLS	FOOTING DRAINING		
Start date	1991	1991	1950's		
Stop date	ONGOING	ONGOING	ONGOING		
Other remediation	OXIDATION				AIR-SPARGING
Start date	?				
Stop date					
In-situ biorem.?					

Seqno	6010005	6010004	6010006	6430009	450001
Facility Type	DOE	DOE	DOE	DOE	DOE
Start/Stop Operations				1967 - 1985	1952 - 1973
Release dates	1960 - 1980's	1960 - 1980's	1964 - 1973		1952/1996
Discov. Date					
Est. mass/vol of release					
DNAPL detected?	YES	NO	NO	NO	
Year monitoring began	1982	1982	1994	1984	
Remed. start	NONE	NONE	NONE	1986 TO 1987	
# yrs. pre-remed. data	16	16	4	1	
# of monitoring wells	48	38		15	
Semi-con. sediments					
Unconsolidated sediments					X
Fractured porous rock	X	X	X	X	
Fractured non-porous rock					
Depth to gw (FT. BGS)	20-Oct	18		10-Apr	
Organic carbon					
Kd or Koc					
Zone confined /unconfined				UNCONFINED	UNCONFINED
Sitewide K (FT/DAY)				0.061	
Low K	0.283	0.4528	1.33E-06	0.001	10
Hi K	12.452	1698	50.94	0.318	24
Geomean K	1.736606587	37.49042292	0.408646017	0.033949604	9.781946493
Stdev K	3.828327561	602.1039246	13.5118717	0.079867438	10.30550015
# K values	13	23	15	13	3
Horiz. grad.(FT/FT)	0.004	0.006	0.003741657	0.02085	0.00175
GW velocity(FT/DAY)	0.1 - 0.33	1.9178		0.00037	
GW flow direction	S/SE	NE	S/SE	SE	SW
Source removed?	NO	NO		YES	YES
Method of removal				TANK & SOIL EXCAVATION	EXTRACTION
Date of removal				1983, 1988	1996
Type of Pump&Treat				1 EXTRACTION WELL	
Start date				1986	
Stop date				6/9/05	
Other remediation					BIOVENTING
Start date				1983	1996
Stop date				1988	
In-situ biorem.?					

<b>Seqno</b>	450003	450005	450004	450002	3902
<b>Facility Type</b>	DOE	DOE	DOE	DOE	DOE
Start/Stop Operations					
Release dates		1951-1973			
Discov. Date					
Est. mass/vol of release		UNK			
DNAPL detected?	YES			NO	
Year monitoring began	1983	1975	1981		1987
Remed. start	1989				1991
# yrs. pre-remed. data	6				4
# of monitoring wells	400	30	100		
Semi-con. sediments					
Unconsolidated sediments	X			X	
Fractured porous rock					
Fractured non-porous rock					
Depth to gw (FT. BGS)					
Organic carbon					
Kd or Koc				KD = 0.00128	
Zone confined /unconfined	CONFINED			UNCONF TO SEMI-CONF	
Sitewide K (FT/DAY)					41
Low K	10			12	
Hi K	50			65	
Geomean K	23.77730992			34.01859413	
Stdev K	15.08973161			24.81330288	0
# K values	5			6	0
Horiz. grad.(FT/FT)	0.06				0.01
GW velocity(FT/DAY)					1.2
GW flow direction	SE				SW
Source removed?	YES				YES
Method of removal	SVE				EXTR WELLS
Date of removal	1993				1991-ONGOING
Type of Pump&Treat	AIR STRIPPER				
Start date	1989			1996	
Stop date					
Other remediation	BIODEGRADATION				
Start date	1996				
Stop date					
In-situ biorem.?	YES				

Seqno	41050002	41350002	2002	3101	3102
Facility Type	DRY CLEANER	DRY CLEANER	DRY CLEANER	GRAIN STORAGE	GRAIN STORAGE
Start/Stop Operations	1940 - PRESENT			1940 - 1985	1962 - PRESENT
Release dates					
Discov. Date	1992				1986
Est. mass/vol of release					
DNAPL detected?	YES	YES			NO
Year monitoring began	1992		1992	1995	1994
Remed. start	1997				NONE
# yrs. pre-remed. data	1			3	4
# of monitoring wells	20			7	7
Semi-con. sediments					
Unconsolidated sediments	X			X	X
Fractured porous rock					
Fractured non-porous rock					
Depth to gw (FT. BGS)				22 - 65	
Organic carbon					
Kd or Koc					
Zone confined /unconfined	UNCONFINED	SEMI-CONFINED		UNCONFINED	UNCONFINED
Sitewide K (FT/DAY)					
Low K	22	0.000368		0.1	2
Hi K	491	0.294		47	80
Geomean K	103.9326705	0.010401538		2.019	16.364
Stdev K	331.6330804	0.207629178		18.051	32.437
# K values	2	2		6	6
Horiz. grad.(FT/FT)		0.01		0.000774597	0.001732051
GW velocity(FT/DAY)					
GW flow direction		S		N	N/NW
Source removed?	NO	YES		NO	
Method of removal		SOIL REMOVAL			
Date of removal		1995			
Type of Pump&Treat	CONTINUOUS OP				
Start date	12/1/96				
Stop date	ONGOING				
Other remediation					
Start date					
Stop date					
In-situ biorem.?	NO			NO	



Seqno	6430007	6380001	4204	41510002	6010008
Facility Type	INDUSTRIAL	INDUSTRIAL	INDUSTRIAL	INDUSTRIAL	INDUSTRIAL
Start/Stop Operations		1929 - 1982	1930 - 1960	1972-1992	1935-PRESENT
Release dates	1964 - 1985				
Discov. Date		1988	1984		
Est. mass/vol of release					
DNAPL detected?			NO	YES	
Year monitoring began	1987	1988	1984	1994	1986
Remed. start	NONE	1991	1985	NONE	NONE
# yrs. pre-remed. data	10	3	14	4	
# of monitoring wells	13	17	52	14	30
Semi-con. sediments					
Unconsolidated sediments		X	X	X	X
Fractured porous rock					
Fractured non-porous rock					
Depth to gw (FT. BGS)				15	
Organic carbon					
Kd or Koc					
Zone confined /unconfined		SEMI-CONFINED		UNCONFINED	
Sitewide K (FT/DAY)		16.6		283	
Low K			0.2		2.3772
Hi K			71		25.187
Geomean K			1.773981143		9.067629331
Stdev K			19.13784762		11.43072465
# K values			14		3
Horiz. grad.(FT/FT)	0.002	0.005	0.023	0.00083666	
GW velocity(FT/DAY)			0.02 - 2.3		
GW flow direction	NE	E/NE	S	N/NW	
Source removed?	NO	YES	NO	NO	
Method of removal		TANK PULLED			
Date of removal		UNKNOWN			
Type of Pump&Treat		INTERIM	INTERIM	NONE	
Start date		1/1/89	1/1/85		
Stop date		4/1/89	1/1/91		
Other remediation					
Start date					
Stop date					
In-situ biorem.?	NO	NO	NO	NO	

Seqno	41470002	6430003	1602	6430011	4202
Facility Type	INDUSTRIAL	INDUSTRIAL	INDUSTRIAL	INDUSTRIAL	INDUSTRIAL
Start/Stop Operations				1969-?	
Release dates	1976 - 1985		1990		
Discov. Date					
Est. mass/vol of release			UNK		
DNAPL detected?	NO		YES		
Year monitoring began	1985	1982	1991		1989
Remed. start	1990			1986	
# yrs. pre-remed. data	5				
# of monitoring wells		37	6		5
Semi-con. sediments					
Unconsolidated sediments	X	X	X		
Fractured porous rock					
Fractured non-porous rock					
Depth to gw (FT. BGS)	10		40		
Organic carbon					
Kd or Koc					
Zone confined /unconfined			CONFINED	CONFINED	UNCONFINED
Sitewide K (FT/DAY)				20	
Low K	0.03		2.04609		0.0003
Hi K	33		31.979		0.6
Geomean K	2.001734418		6.580809778		0.023335639
Stdev K	10.7148196		21.16576364		0.981563738
# K values	13		2		9
Horiz. grad.(FT/FT)	0.026		0.01		0.14
GW velocity(FT/DAY)	1.56			15GPM	
GW flow direction	NE		NW		NW
Source removed?	YES	YES		YES	NO
Method of removal	SOIL REMOVAL			TANKS/SOIL REMOVAL	
Date of removal	UNKNOWN			1984/1989	
Type of Pump&Treat	CONTINUOUS OP				SHORT-TERM
Start date	1/1/90				10/1/94
Stop date	ONGOING				3/1/95
Other remediation					
Start date					
Stop date					
In-situ biorem.?					

<b>Seqno</b>	6430002	6430001	6370001	6430005	6490001
<b>Facility Type</b>	INDUSTRIAL	INDUSTRIAL	INDUSTRIAL	INDUSTRIAL	INDUSTRIAL
Start/Stop Operations	1965 - 1980	1976 - PRESENT		1947-1987	1959-?
Release dates	1968 - 1982	1976 - 1985	1953-1983	1978 - 1987	
Discov. Date		1982			
Est. mass/vol of release			850-1700KG TCE		
DNAPL detected?	NO		NO	NO	YES
Year monitoring began	1981	1976	1987	1988	1988
Remed. start	1982	1985	NONE	1992	1990
# yrs. pre-remed. data	1	9		5	2
# of monitoring wells	35	17		10	90
Semi-con. sediments					
Unconsolidated sediments	X	X	X	X	X
Fractured porous rock					
Fractured non-porous rock					
Depth to gw (FT. BGS)	18.5	10 - 20.5		20-22	3
Organic carbon					0.5-soil
Kd or Koc					
Zone confined /unconfined	UNCONFINED	CONFINED	UNCONFINED	SEMI-CONFINED	UNCONF TO SEMI-CONF
Sitewide K (FT/DAY)		113.2	10	0	
Low K	39			0	2
Hi K	42			0	10
Geomean K	40.47221269			0	4.472135955
Stdev K	2.1213			0	
# K values	2			0	
Horiz. grad.(FT/FT)	0.36	0.005	0.015	0.0015	0.006529931
GW velocity(FT/DAY)	0.56	2.15	0.6		0.1-6.9
GW flow direction	N	NE	W/NW	N	SW
Source removed?	YES	NO	Y	PARTIAL?	YES
Method of removal	SOIL REMOVAL		SUMP/SOIL SYS REMOVAL		GW EXT/STORM DRAIN
Date of removal	1981 & 1985		1988		1990 & 1992
Type of Pump&Treat	INTERIM	CONTINUOUS OP			EXTRACTION WELLS
Start date	1/1/82	2/1/85		1992	1990
Stop date	?	7/1/93			ONGOING
Other remediation					
Start date					
Stop date					
In-situ biorem.?	YES				

Seqno	41050003	41470001	1703	6490001	6430006
Facility Type	INDUSTRIAL	INDUSTRIAL	INDUSTRIAL	INDUSTRIAL	INDUSTRIAL
Start/Stop Operations	?	LATE 1950'S-1989	1898 - 1982	1950 - 1986	? - 1985
Release dates		1950-1989			
Discov. Date		1991			
Est. mass/vol of release		0-100 GAL/YR			
DNAPL detected?		YES		YES	
Year monitoring began	1992	1989 OR 1992		1989	1985
Remed. start				1994	1985
# yrs. pre-remed. data		28		5	
# of monitoring wells				35	31
Semi-con. sediments					
Unconsolidated sediments	X	X	X	X	X
Fractured porous rock					
Fractured non-porous rock					
Depth to gw (FT. BGS)	9-Feb	10-Mar		10-Aug	
Organic carbon		20-500PPM			
Kd or Koc					
Zone confined /unconfined		SEMI-CONFINED	SEMI-CONFINED	UNCONFINED	CONFINED
Sitewide K (FT/DAY)		3.4			
Low K	0.2		0.03	2	
Hi K	9		368	10	
Geomean K	1.341640786	2.001734418	4.09554	4.472135955	
Stdev K	6.222539674	10.7148196	119.0204	5.656854249	
# K values	2		12	2	
Horiz. grad.(FT/FT)	0.012	0.0045	0.04	0.006529931	0.00244949
GW velocity(FT/DAY)					
GW flow direction	W/NW	NW	E/SE	SW	N/NE
Source removed?		NO		YES	YES
Method of removal				DEBRIS & SOIL REMOVAL	TANK PULLED/SVE
Date of removal				1998/99	1985/1987
Type of Pump&Treat				13 EXTRACTION WELLS	EXTR WELL/AIR STRIP
Start date				1994	1987
Stop date					ONGOING
Other remediation					
Start date					
Stop date					
In-situ biorem.?					

Seqno	6190002	41050001	41350001	401	1601
Facility Type	INDUSTRIAL	INDUSTRIAL	INDUSTRIAL	LANDFILL	LANDFILL
Start/Stop Operations			1931-1992		1955-1993
Release dates		1970-1990	1959-1992		
Discov. Date		1992			
Est. mass/vol of release			UNK		
DNAPL detected?		NO	YES	NO	YES
Year monitoring began	1989	1992	1994	1988	1992
Remed. start		1994	1996	1989	
# yrs. pre-remed. data		2	2	1	
# of monitoring wells	20	25	30	62	5
Semi-con. sediments				X	
Unconsolidated sediments		X		X	
Fractured porous rock					
Fractured non-porous rock					X
Depth to gw (FT. BGS)			12-May	25 - 65	
Organic carbon			<0.1% TOC		
Kd or Koc					
Zone confined /unconfined		SEMI-CONFINED	UNCONFINED	UNCONF TO SEMI-CONF	
Sitewide K (FT/DAY)				217	
Low K	0.3	360	5.4		0.0112917
Hi K	110	540	141		4.5846
Geomean K	11.86573051		49.90752		0.226116823
Stdev K	35.28851973		56.50212		3.193795068
# K values	16		5	7	2
Horiz. grad.(FT/FT)	0.004	0.005	0.027333	0.002901763	
GW velocity(FT/DAY)		0.9452	0.4		
GW flow direction	E/NE	NW	W/SW	W/SW	
Source removed?		YES	NO		NO
Method of removal	TANK REMOVAL/SUMP/SVE				
Date of removal		95/94			
Type of Pump&Treat					
Start date					
Stop date					
Other remediation			SVE		NO
Start date			Jun-96		
Stop date			Sep-96		
In-situ biorem.?					NO

<b>Seqno</b>	1603	41330001	41290001		
<b>Facility Type</b>	LANDFILL	LANDFILL	TRUCK SPILL		
Start/Stop Operations		1967-PRESENT			
Release dates	1972-1993?		1984		
Discov. Date			1984		
Est. mass/vol of release	UNK	UNK	300g-acetone/700g TCA		
DNAPL detected?	NO	NO	YES		
Year monitoring began	1990	1989	1985		
Remed. start	NONE	1994			
# yrs. pre-remed. data		5	10		
# of monitoring wells	23	33	28		
Semi-con. sediments					
Unconsolidated sediments		X	X		
Fractured porous rock					
Fractured non-porous rock		X			
Depth to gw (FT. BGS)		40	20		
Organic carbon					
Kd or Koc					
Zone confined /unconfined			UNCONF TO SEMI-CONF		
Sitewide K (FT/DAY)		3.4			
Low K	0.8		7.8		
Hi K	23.1		180		
Geomean K	4.23		37.46998799		
Stdev K			121.7637877		
# K values			2		
Horiz. grad.(FT/FT)	0.067082039	0.05	0.003		
GW velocity(FT/DAY)					
GW flow direction	SW	N	NE		
Source removed?	NO		YES		
Method of removal			SVE		
Date of removal					
Type of Pump&Treat		MIGRATION CONTROL	MIGRATION CONTROL		
Start date		1994	10/1/94		
Stop date			ONGOING		
Other remediation	NO				
Start date					
Stop date					
In-situ biorem.?	NO				

# **Appendix G**

## **Probabilistic Plume Modeling**

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## Appendix G

### Probabilistic Plume Modeling

#### G-1. Overview

The trends observed in the statistical evaluations of the field data, while intuitive, are empirical owing to the nature of the analyses. Reconciliation of these empirical findings with conceptual mathematical models of plume behavior can provide a theoretical basis for interpreting the observations. Given the emphasis of the present study on identifying and quantifying relationships between averaged site hydrogeologic variables and plume variables defined in a broad context, analytical solutions are highly suitable models for a probabilistic approach. They also produce simplified representations of plume behavior that are readily amenable to statistical analyses. In this context, the heterogeneity in the groundwater flow field, which often severely limits the application of analytical solutions, may be addressed through the macrodispersion coefficients.

Domenico (1987) presented a solution for concentration,  $C$ , as a function of  $x$ ,  $y$ , and  $t$ , which also accounts for the effects of dispersion in the vertical direction:

$$C(x,y,t) = \left(\frac{C_0}{8}\right) \exp\left\{\left(\frac{x}{2\alpha_x}\right)\left[1 - \left(1 + \frac{4R\lambda\alpha_x}{v}\right)^{1/2}\right]\right\} \cdot \operatorname{erfc}\left[\frac{x - \frac{v}{R}t(1 + 4R\lambda\alpha_x/v)^{1/2}}{2\left(\alpha_x \frac{v}{R}t\right)^{1/2}}\right] \quad (\text{Eq. G-1})$$

$$\cdot \left\{\operatorname{erf}\left[\frac{(y + Y/2)}{2(\alpha_y x)^{1/2}}\right] - \operatorname{erf}\left[\frac{(y - Y/2)}{2(\alpha_y x)^{1/2}}\right]\right\} \cdot \left\{\operatorname{erf}\left[\frac{Z}{2(\alpha_z x)^{1/2}}\right] - \operatorname{erf}\left[\frac{-Z}{2(\alpha_z x)^{1/2}}\right]\right\}$$

Here,  $C_0$  refers to a vertical rectangular-source (dimension  $Y \times Z$ ), of solute concentration along the upstream boundary,  $v$  the uniform groundwater velocity in the  $x$ -direction,  $\alpha_x$ ,  $\alpha_y$ , and  $\alpha_z$  the respective longitudinal, transverse, and vertical transverse dispersivities,  $R$  the retardation coefficient, and  $\lambda$  the first-order transformation rate. This solution is only valid for a semi-infinite homogeneous aquifer. From Eq. G-1, the plume's length along the  $x$ -axis may be estimated by setting  $y = 0$  and  $C$  equal to some specific contour interval (i.e.,  $C = 10$  ppb), and solving for  $x$  using a suitable numerical approach (in this case a bisection search algorithm).

Application of Monte Carlo simulation techniques to analytical solute transport models can provide valuable insights into factors affecting plume behavior when combined with population studies of existing groundwater plumes. Monte Carlo analyses are routinely used in engineering probability forecasting applications (e.g., Ang and Tang, 1984). Woodbury et al. (1995) discussed the use of Monte Carlo analyses in practical ground water engineering applications. The main reason for resorting to a probabilistic analysis of phenomena of transport making use of a mathematical model stems from the lack of sufficient field data on site-specific features of plume

behavior. Probabilistic modeling of contaminant transport involves utilizing user-specified probability distributions of physical and chemical model variables, based on available data, to produce forecasts through multiple Monte Carlo realizations. The Monte Carlo approach allows uncertainties in hydrogeological data (e.g., hydraulic conductivity, hydraulic gradient (magnitude and direction), nature of the source, and chemical data (e.g., degradation rates) to be translated into uncertainties regarding plume extents and rates of growth. Sensitivity analyses based on comparing uncertainties in input variables to the variance in corresponding forecast results may provide insight into the critical data for quantifying the behavior of plumes.

## G-2. Parameter Distributions

For the modeling analysis, synthetic plumes were generated using random combinations of the variables in Eq. G-1. The values of these variables were constrained by probability distributions developed from field data (Table G-1). Probability distributions of groundwater velocity were obtained by Darcy's law for ranges of  $K$  and  $\nabla h$  values noted at sites included in the study. Similarly, a probability distribution for  $C_0$  could be estimated from the ranges of maximum historical concentrations. In this case, values of  $C_{max}$ , representing maximum measured concentrations, were chosen from the overall  $C_{max}$  probability distribution observed in the field data set. For each synthetic plume realization, this value was assumed to represent 10% of the actual boundary concentration,  $C_0$ , based on the 10% saturation rule-of-thumb for inferring the presence of DNAPL (Feenstra and Cherry, 1988). Thus the geometric mean value of the  $C_0$  probability distribution is a factor of ten higher than the  $C_{max}$  distribution, although the standard deviation is identical.

Ranges of other variables (e.g.,  $R$ ,  $\alpha_x$ ,  $\alpha_y$ ,  $t$ ), while not well-constrained by the database, can be assumed within reason using best professional judgment. The retardation coefficient,  $R$ , for example, may be calculated from the relationship,

$$R = 1 + \frac{K_{oc} f_{oc} \rho_b}{\phi} \quad (\text{Eq. G-2})$$

where  $K_{oc}$  is the organic carbon partitioning coefficient,  $f_{oc}$  is the fractional organic carbon content,  $\rho_b$  the bulk density, and  $\phi$  the porosity. The probability distribution of  $f_{oc}$  could not be determined from the site database because of a paucity of data. Instead, a probability distribution was postulated (Fig. G-1) from a published distribution of  $f_{oc}$  values observed at a number of field sites (Wiedemeier et al., 1997). First-order degradation rates ranging from  $\lambda = 0.7$  to  $\lambda = 0.07 \text{ year}^{-1}$ , corresponding to half-lives from 1 year to 10 years, were chosen from an informal survey of reported values in the literature (the survey of reductive dehalogenation rates of TCE by Aronson and Howard (1997) recommends half-lives of 1.2 years to 13.2 years as conservative estimates). Half of the synthetic plumes were assigned degradation rates within this range, while the remainder of the plumes were assigned a degradation rate of  $\lambda = 0$  as a control set representing stable CVOCs.

### G-3. Model Results

The output of the Monte Carlo simulations consisted of a distribution of plume lengths, each corresponding to a unique set of random input variables chosen from the defined probability distributions. A total of 2000 realizations were developed. To mimic the results of the field data analyses as much as possible, only simulated plumes with lengths falling within the range of observed plume lengths (approximately 100 feet to 10,000 feet) were included in the analysis. To simulate the size of the field data set, 100 plumes were drawn at random from the transforming population and the stable population each. Relationships between plume length and  $C_{max}$  (assumed equal to 1/10 the  $C_0$  value for each realization) as well as plume length and specified site groundwater velocity,  $v$ , are shown for all synthetic plumes on Figures G-2 and G-3, respectively. The scatter evident in both relationships illustrates the effect of multiple variables on plume length, even under ideal conditions (uniform groundwater velocity field, Fickian-type dispersion, uniform transformation rate, isotropic two-dimensional aquifer, and constant boundary conditions). The relationship between plume length and  $C_{max}$  reproduces the scatter observed in the field data fairly well (Appendix A, Fig. A-1). In contrast, much more scatter is evident in the field data with respect to the plume-length-versus-velocity relationship (Appendix A, Fig. A-3) than in the simulated plume set. The explanation for this difference is likely to stem from the difficulty in defining a mean site groundwater velocity for a real field site, in contrast to the specified (known) uniform velocities characterizing the synthetic plumes.

Synthetic plume length distributions for transforming and stable CVOC plumes are shown on Fig. G-4 (top). These results are very similar to analysis of the field data; transformations appear to exert little influence on raw plume lengths above the noise in the data caused by other factors. However, the definition of a plume length index for the synthetic plumes in a manner analogous to the measured plume lengths (Appendix A, Eq. A-1) produces a significant separation of the two probability distributions (Fig. G-4, bottom). This analysis procedure and the results are consistent with those associated with the field data. The findings thus support the conclusion that source strength and groundwater velocity exert a strong enough influence on plume length to be directly discernible. In contrast, transformation rates are slow enough so that plume length effects cannot be easily identified above the noise associated with plume data without normalization procedures.

Rank-based correlation coefficients quantifying the relationships between plume length, the plume length index as defined in Appendix A, and the various model variables are shown in Table G-2. The correlation coefficients indicate the importance of groundwater velocity variability and variability in the boundary concentration in influencing plume length relative to other variables. Dividing plume length by  $v$  and  $C_{max}$  reduces the effects of these two variables, so that the correlations between other variables such as  $\lambda$  and the plume length index improve. This may explain why the plume length index concept is successful at identifying differences between the plumes from the No RD and Strong RD groups; the indexing procedure improves the correlation of plume extent with the rate of transformation.

Best-fit lognormal frequency distributions of input parameters (maximum concentration and groundwater velocity) and output metrics (plume length and plume length indices) are shown on Figure G-5 for the synthetic plume population, with the same distributions gleaned from the field data shown as a summary comparison. The capacity of the model to capture the average behavior of plumes in the data set is encouraging, providing support to the notion that site-specific effects tend to average out over a large number of sites, so that general trends do become apparent.

Ultimately, the modeling results, the field data, and the general linear model development (Appendix C) all convey the possibility of examining plume populations as multivariate systems (Figs. G-6 and G-7). Models of such systems would link measurable aspects of plume behavior, such as length, to linear combinations of variables (or log variables) in a statistical sense. Powerful new insights could be gleaned into plume behavior, provided that a large enough data set could be assembled to allow analyses of distinct regions of variable space. In the examples given in Figs. G-6 and G-7, the multivariate relationship between plume length, groundwater velocity, and maximum concentration suggests a much stronger role for velocity in influencing plume length in the synthetic plume population than in the field data. This may stem from a deficiency in our capacity to accurately quantify a true mean groundwater velocity for field sites, as the modeled plumes are all based on an assumption of a uniform flow field which is known precisely. As such, this may suggest the need to use geostatistical approaches in future analyses which quantify the uncertainties associated with groundwater velocity at field sites in the data set.

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Table G-1. Transport model parameter probability distributions.

Parameter	Distribution	Basis
Maximum concentration (ppb), $C_0$	Lognormal. 10th-percentile: 29 90th-percentile: 23,750	Lognormal distribution fit to observations, uniformly multiplied by 10.
Source area width (ft), $Y$	Uniform. 5-60	Postulated.
Source area depth (ft), $Z$	Uniform. 5-60	Postulated.
Hydraulic conductivity (ft/day), $K$	Lognormal. 10th-percentile: 0.19 90th-percentile: 246	Lognormal observations fit to geometric mean values from each site <sup>1</sup> .
Hydraulic gradient, $\nabla h$	Lognormal. 10th-percentile: 0.0011 90th-percentile: 0.0614	Lognormal observations fit to reported values from each site
Porosity, $\phi$	Normal. $0.25 \pm 0.03$	Postulated.
Fractional soil organic carbon, $f_{oc}$	Lognormal. 10th-percentile: 0.01% 90th-percentile: 1%	Postulated.
Transformation half-life (yrs), $t_{1/2}$	Uniform. 1-10	Postulated; based on an informal review of literature values.
Ratio of longitudinal dispersivity, $\alpha_x$ , to plume length	Lognormal. 10th-percentile: 0.033 90th-percentile: 0.33	Postulated; based on the common assumption of the ratio of $\alpha_x$ to plume length ~ 10%.
Ratio of longitudinal dispersivity, $\alpha_y$ , to plume length	Lognormal. 10th-percentile: 0.0033 90th-percentile: 0.033	Postulated; based on the common assumption of the ratio of $\alpha_y$ to $\alpha_x$ ~ 10%.
Ratio of longitudinal dispersivity, $\alpha_z$ , to plume length	Lognormal. 10th-percentile: $1.67 \times 10^{-3}$ 90th-percentile: $1.67 \times 10^{-2}$	Postulated.
Elapsed time since release (yrs), $t$	Uniform. 10-50	Postulated; informally based on typical reported site use histories.

<sup>1</sup>Based on reported pumping test or slug test results.

**Table G-2. Rank correlation coefficients (Spearman's  $r$ ) between simulated plume length and plume length indices and model variables.**

Variable	Rank correlation coefficient with respect to L	Rank correlation coefficient with respect to PLI
Groundwater velocity, $v$	0.73	—
Maximum concentration, $C_{max}$	0.32	—
Retardation coefficient, $R$	-0.20	-0.32
Ratio of vertical dispersivity to plume length, $\alpha_z:L$	-0.20	0.06
First-order degradation coefficient, $\lambda$	-0.12	-0.21
Ratio of longitudinal dispersivity to plume length, $\alpha_x:L$	0.06	0.15
Transverse extent of source area, $Y$	-0.04	0.25
Vertical extent of source area, $Z$	-0.04	0.18
Ratio of transverse dispersivity to plume length, $\alpha_y:L$	-0.01	-0.16
Elapsed time since source term initiation, $t$	0.00	-0.01

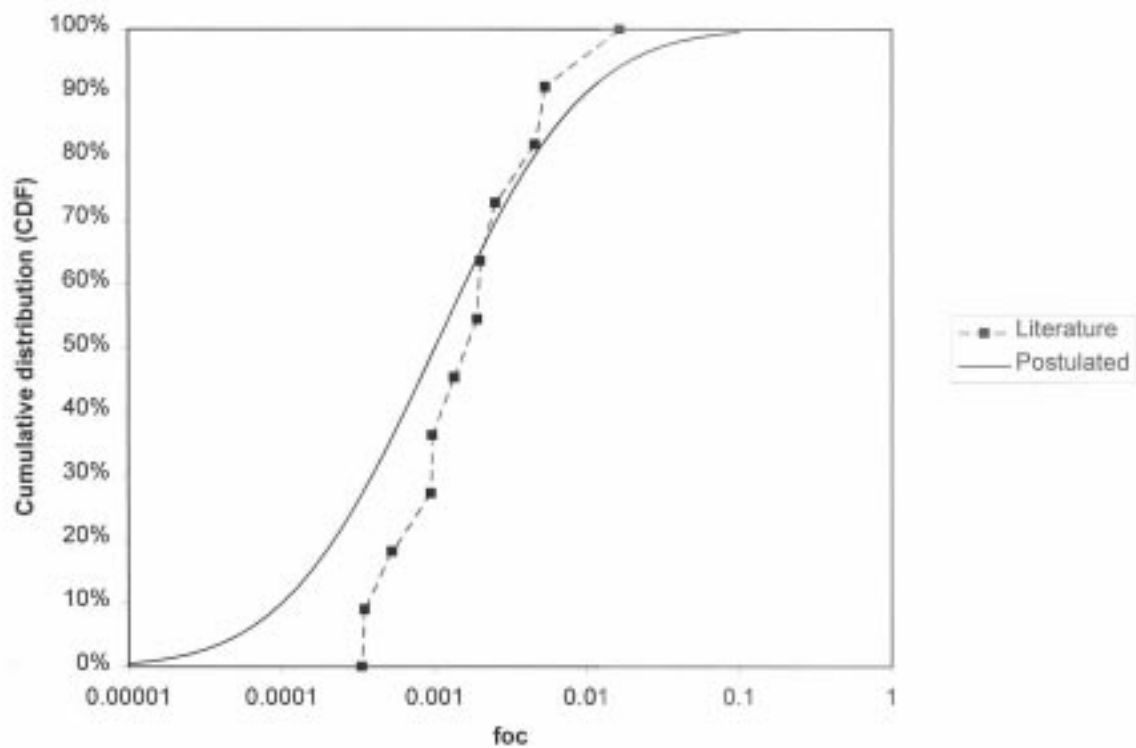


Figure G-1. Cumulative distributions of organic carbon content developed from analysis of reported field measurements (Weidemeier et al., 1997) and the lognormal distribution used in the Monte Carlo plume simulations.

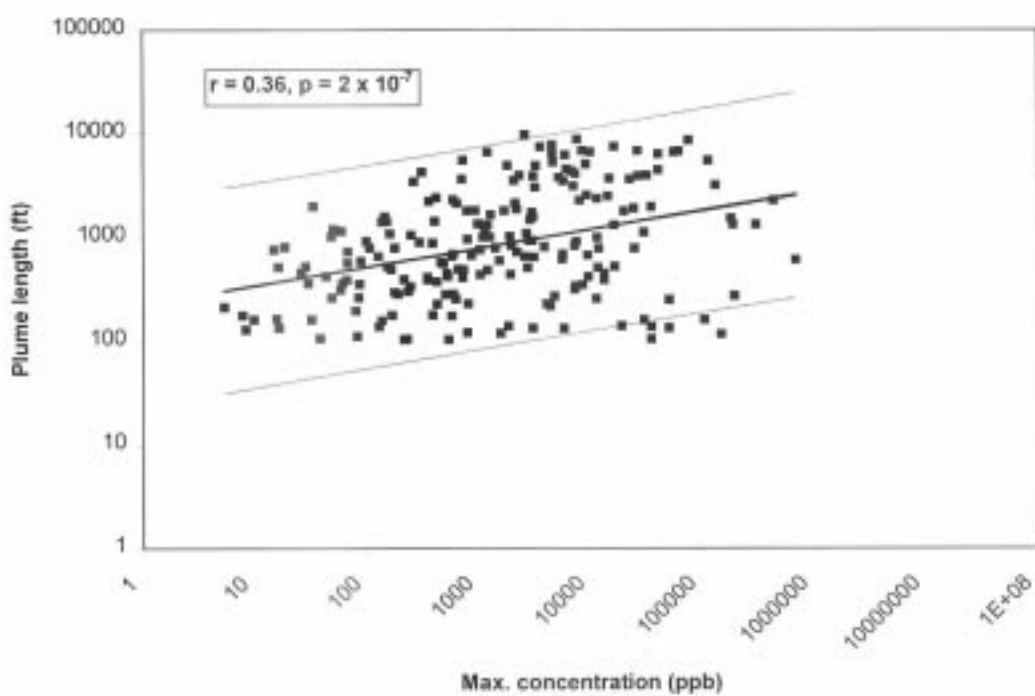


Figure G-2. Relationship between log plume length and log  $C_{max}$  for the synthetic 10-ppb plume population. Dashed lines denote the 95% prediction confidence band.



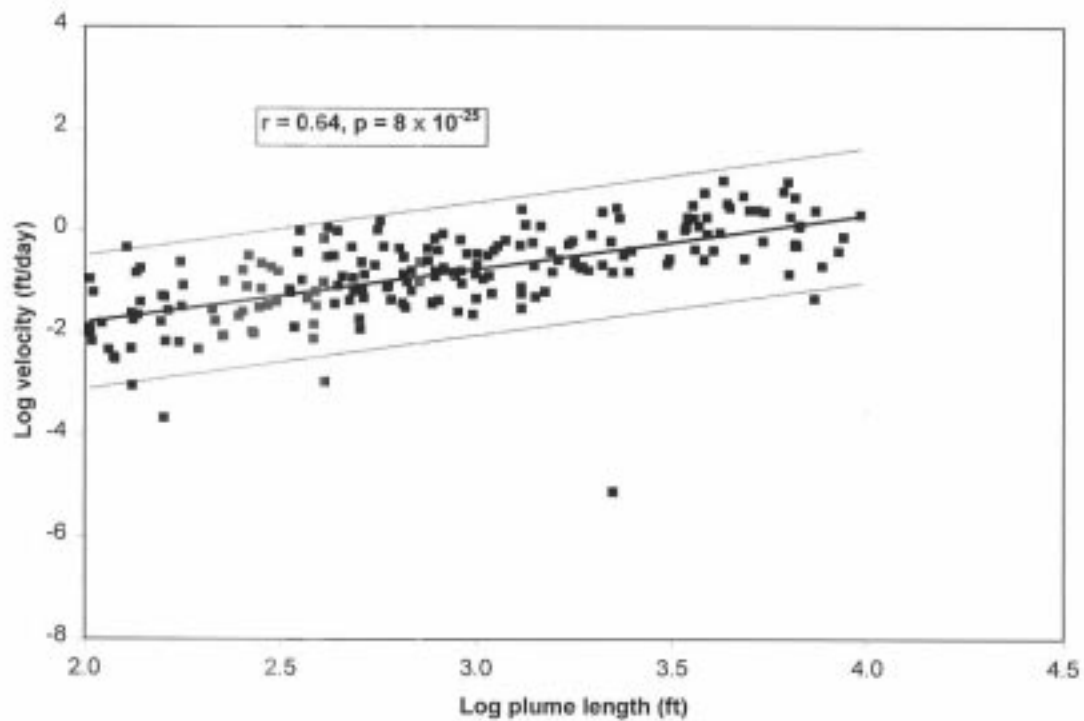


Figure G-3. Relationship between log plume length and log specified  $v$  from the synthetic plume. The independent variable, log  $v$ , is plotted on the y-axis to maintain consistency with Figure A-4. Dashed lines denote the 95% prediction confidence band.

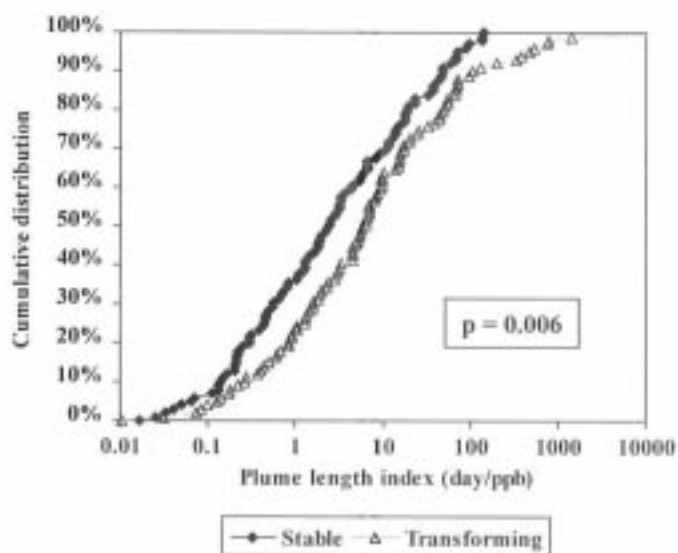
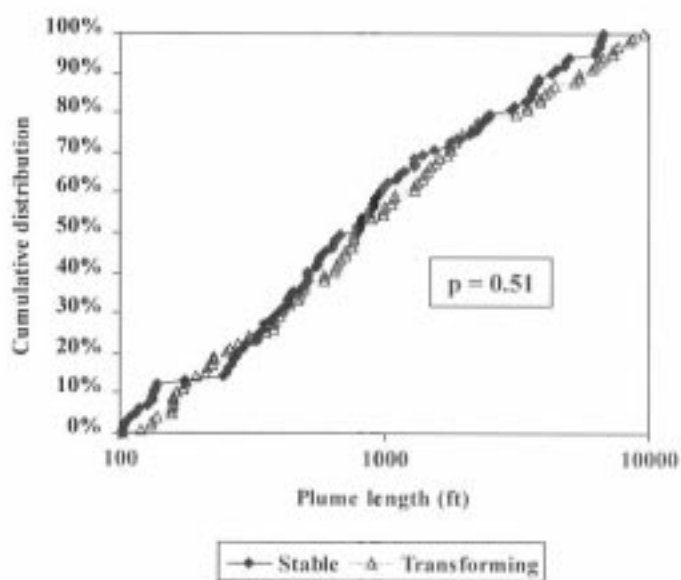


Figure G-4. Cumulative distributions of plume lengths for synthetic stable and transforming plumes (top), and distributions of plume length indices (bottom).  $P$ -values refer to the null hypothesis probability (i.e. the probability that the two data sets have equal geometric means).

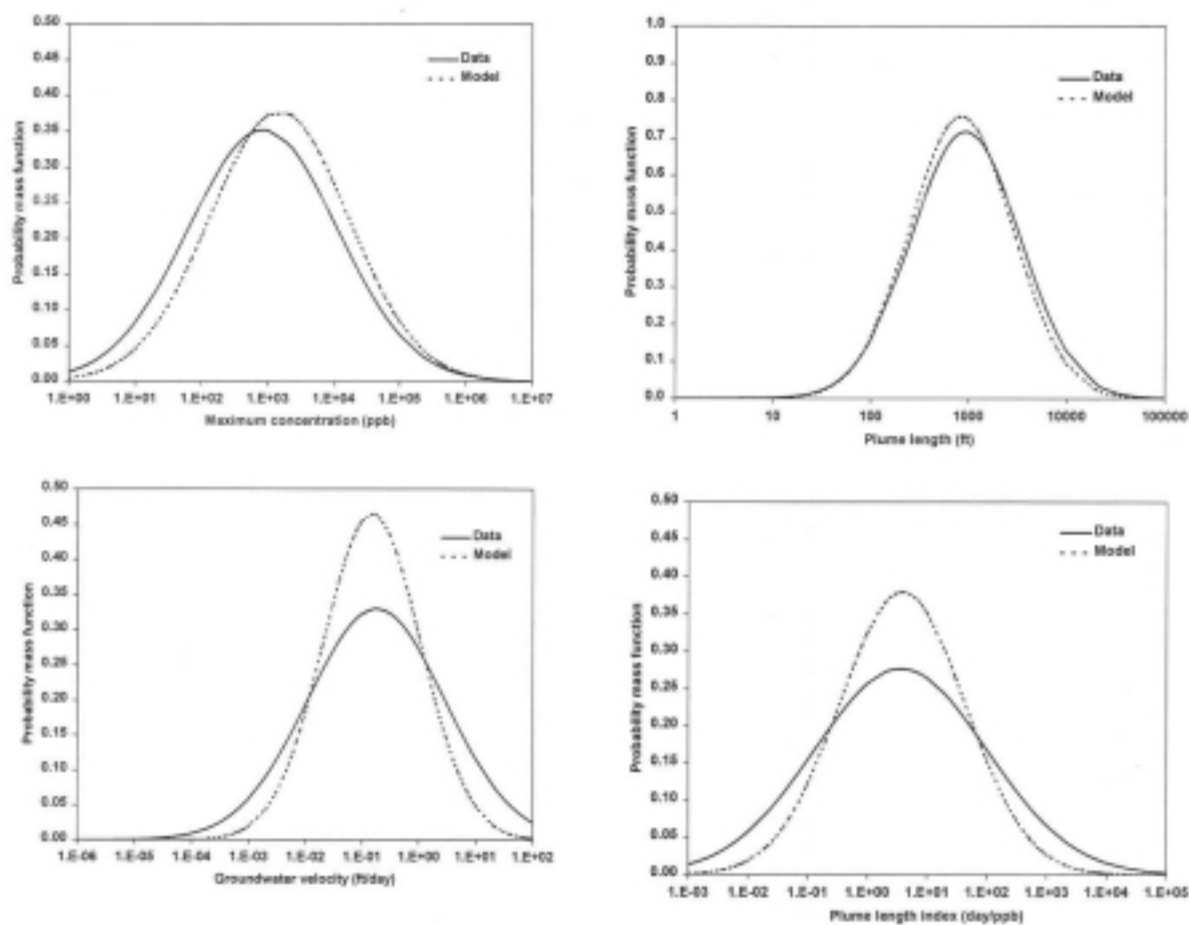
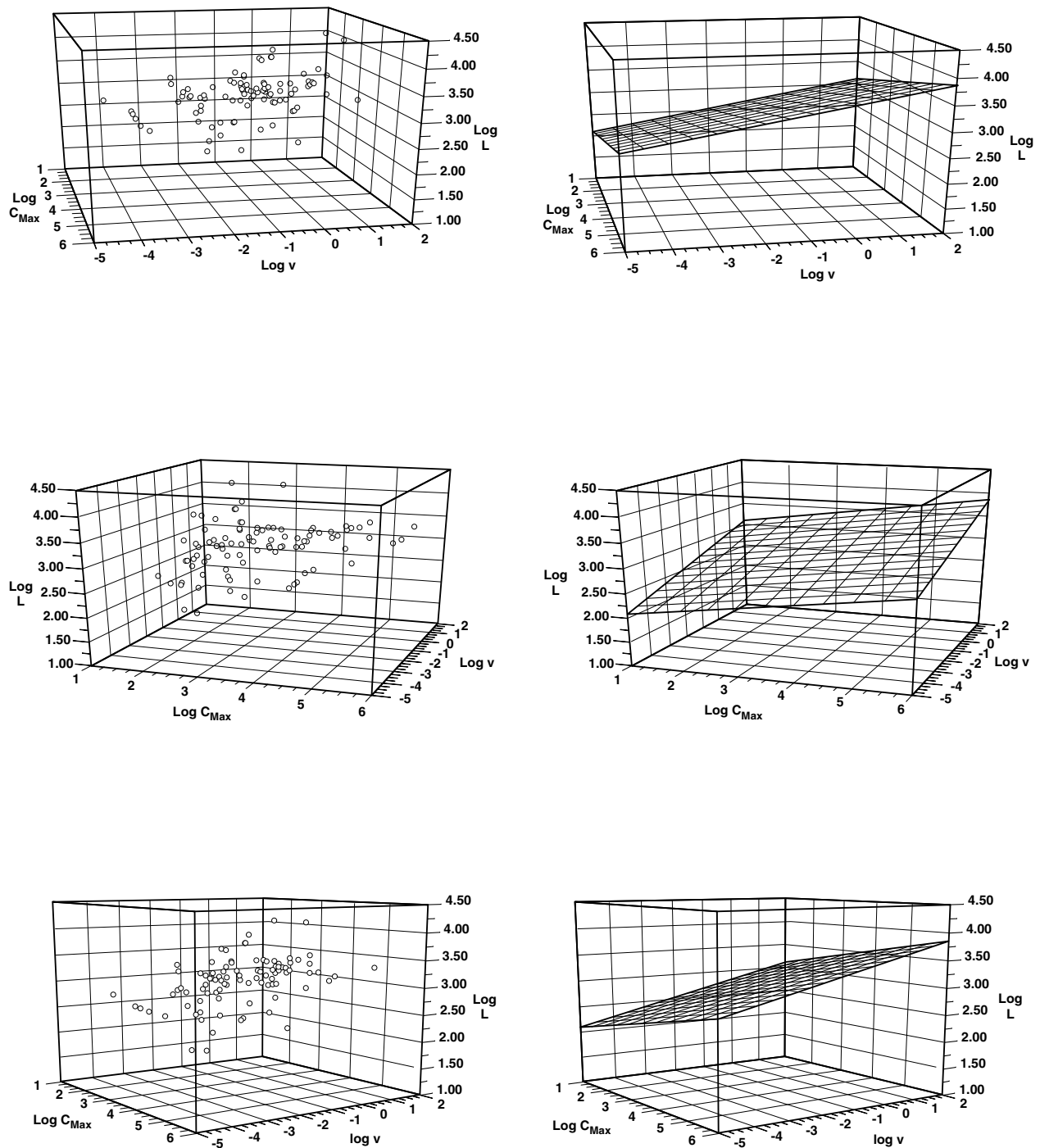
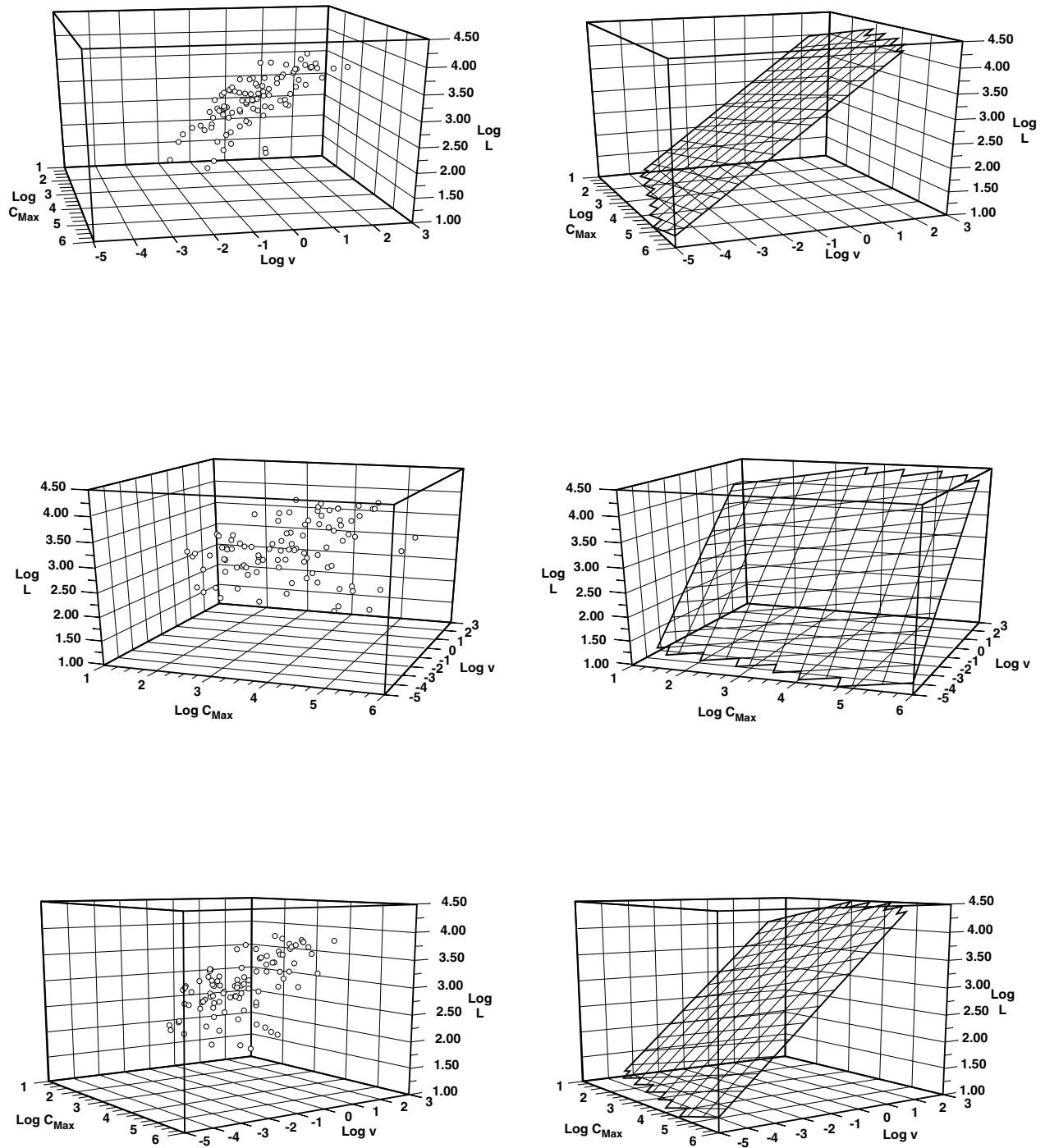


Figure G-5. Lognormal probability distributions for independent variables (maximum concentration and groundwater velocity) and dependent variables (plume length – 10 ppb – and plume length index) fit to the CVOC historical case data (“Data”) and the synthetic plume population (“Model”).



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Figure G-6. Multivariate relationship between log hydraulic conductivity, log maximum historical concentration, and log plume length for measured data (viewed from multiple angles). Biotransformation was eliminated as a variable in this scatter plot by plotting only plumes from the No-RD group. Multivariate correlation coefficient:  $r = 0.48$  (corresponding best-fit planar surface shown in right column).



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Figure G-7. Multivariate relationship between log hydraulic conductivity, log maximum historical concentration, and log plume length for synthetic plume population (viewed from multiple angles). Degradation was eliminated as a variable in this scatter plot by plotting only those plumes that were assigned a value of  $\neq 0$ . Multivariate correlation coefficient:  $r = 0.83$  (corresponding best-fit planar surface shown in right column).



## **Appendix H**

### **Use of Probability Distributions of the CVOC Plume Length Index as a Reference Frame for Plume Behavior**





## Appendix H

### Use of Probability Distributions of the CVOC Plume Length Index as a Reference Frame for Plume Behavior

The analyses conducted in this study suggest that creation of a Plume Length Index (PLI) through the normalization of plume length by maximum concentration and site mean hydraulic conductivity provides a means for identifying the effects of transformation and partitioning processes on plume behavior. As such, the distribution of PLI may serve as a reference frame for classifying plume sizes. This probability distribution of PLI is shown on Figure H-1. “Typical” plumes fall, by definition, near the 50th percentile of the distribution. PLIs falling into the low-end tail of the distribution would be characterized as “short” for the given environment, based on comparison to other plumes. Conversely, PLIs falling into the high-end tail would be characterized as atypically “long”.

This classification scheme may provide a systematic means for identifying anomalous plumes and may be used to quantify the effects of reductive dehalogenation, transport through fractured rock settings, pumping from nearby water supply wells, and other factors which could potentially influence plume length. To test this concept, plume analyses were conducted on 32 plumes from eight sites that were not included in the 65 sites constituting the kernel of the database. These sites were not included in the original analyses because data did not become available until late in the study. As such, these eight sites represent a random sample of environmental conditions in the same manner as any of the 65 sites included in the original analyses.

Individual PLIs by CVOC from each of the eight sites are shown on Figure H-2 along with the PLI cumulative distribution derived from analyses of the original 65 sites (i.e., the kernel population). The logarithms of the PLIs associated with each of the eight sites were compared to those of the original data set using the student's *t*-test as a means for identifying sites featuring plumes that differed significantly (i.e., exceeding the 95% confidence level) from the kernel population. Among the 8 sites, five were characterized by plumes that did not differ significantly from the kernel population in terms of PLI. Two of the sites, Seq. No. 6340001 and Seq. No. 4902, appeared to be characterized by PLIs significantly longer than the kernel population, whereas a single site, Seq. No. 6380006, exhibited significantly shorter PLI. In the case of Site 6380006, strong evidence of reductive dehalogenation exists, with a vinyl chloride plume present along with co-contamination by fuel hydrocarbons. At the only site among the 8 exhibiting strong evidence of reductive dehalogenation, the lower PLI is consistent with the analyses discussed earlier in this report. Contour mapping of CVOC concentration data associated with Site 6340001 (see Figure H-3) reveals that several distinct plumes are discernible in the site database. The plume algorithm (described in Appendix B) was unable to differentiate the individual plumes and interpreted the data as a single continuous plume, resulting in a PLI that is indicative of a distinctly long plume. Normally, the data collection procedures (Chapter 2) would have identified such distinct plumes and labeled them as such, preventing such problems.

Nevertheless, although this example represents an error in the processing of site data in this instance, it does point out the utility in using the PLI distribution as a reference frame for identifying anomalies. In the case of Site 4902, a satisfactory explanation for the atypically long normalized plume lengths could not be found. Given the mean hydraulic conductivity of 1.7 ft/day at this site, the 3,000-ft-long TCE plume length is unusual for the maximum historical concentration of only 350 ppb. It is possible that in this case higher source area concentrations, which would reduce the PLI, may have existed in the past and dispersed or else were not detected by the monitoring well network.

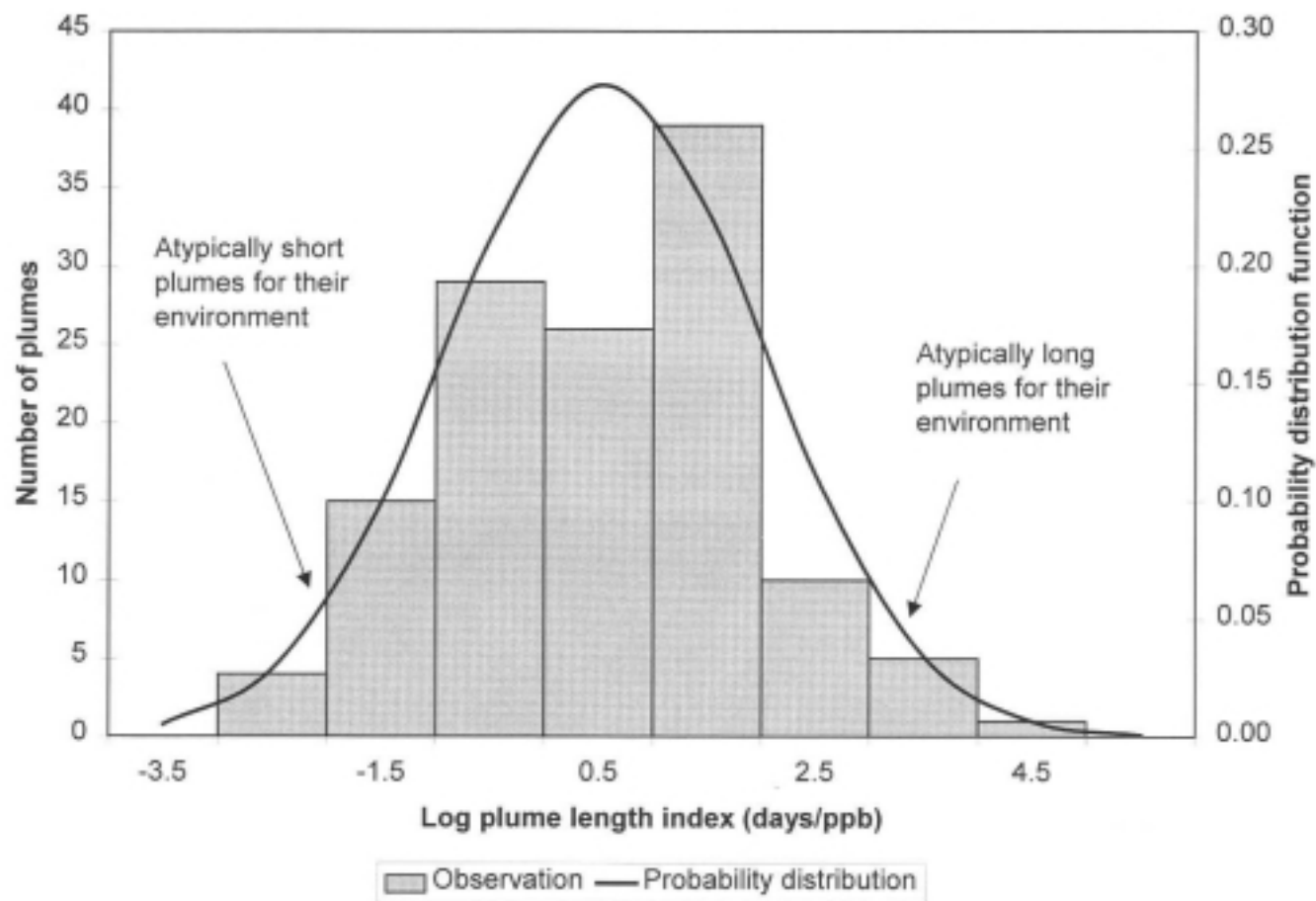


Figure H-1. Histogram and best-fit lognormal probability distribution of CVOC plume length indices (plume length divided by the product of the maximum concentration and groundwater velocity).

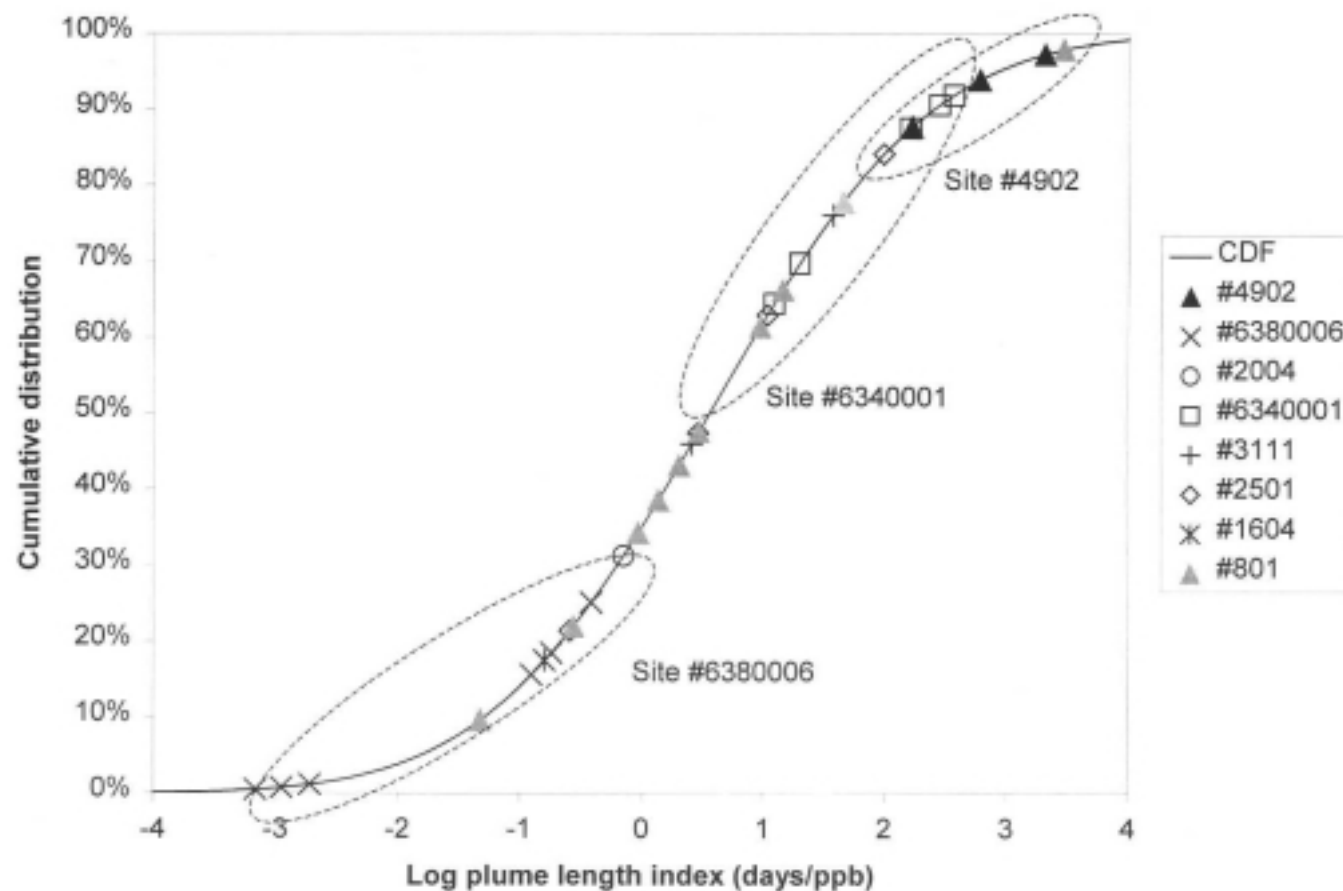


Figure H-2. Plume length indices for 8 test sites beyond the 65 kernel CVOC sites in the data set. The cumulative distribution function (CDF) best-fit to the kernel data set is shown for comparison.

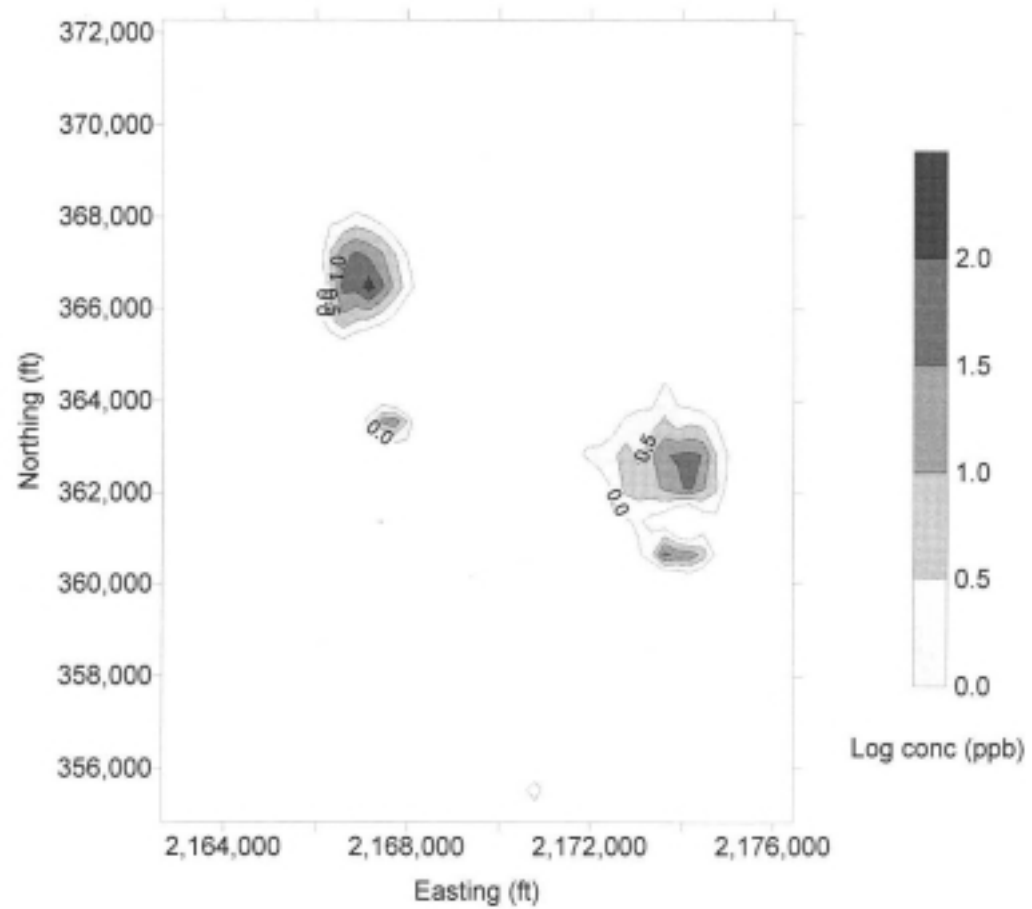


Figure H-3. 1,1-DCE plumes at Site 6340001.